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# Dynamic Simulation of the Lurgi-type Reactor for Methanol Synthesis

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The purpose of this work is to develop a reasonably detailed dynamic model of a Lurgi-type industrial methanol synthesis reactor so as to determine important simplifications, to identify application/operating model limits, and to preliminary check the feasibility for the Nonlinear Model Predictive Control (NMPC) methodology. To do so, a Partially Differential Equation (PDE) system is formulated and integrated to characterize the main phenomena occurring in this shell and tube boiler-reactor. The PDE numerical solution is performed via certain very performing algorithms (BzzMath library).

## 1. Introduction

The present paper focuses the attention on the dynamic modeling and control of a synthesis reactor of methanol from natural gas, via syngas (CO and $H_2$ mixture) obtained by means of steam reforming operations (Lange, 2001; Olah et al., 2009). The synthesis reactor is crucial to the overall process because of its intrinsic nonlinearity and the complex phenomena involved, especially in the fixed-bed Lurgi-type reactor (Lurgi GmbH, 2009) that we selected to be in line with the current trend for shell and tube reactor- boilers to be used in large-scale plants (Manenti et al., 2011). This special configuration sees the tube side filled with catalyst for the synthesis reactions, whereas the shell side is fed by water to regulate the reactor temperature and generate high-pressure steam.
The dynamic modeling leads to a Partial Differential Equation (PDE) system, traditionally hard to solve from a computational point of view (Logist et al., 2009). It is therefore necessary to implement a series of model formulations (parabolic and hyperbolic) and to investigate the computational effort required to integrate the dynamic model, especially regarding the need of very high numerical performances for the implementation of certain nonlinear model predictive control techniques (Manenti et al., 2009a; Dones et al., 2010; Manenti, 2011) in the next works.

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## 2. Model

Methanol synthesis reactors are particularly hard to model as they involve at least four significant dimensions through which the system might evolve: (I) the axial direction of the reactor; (II) the radial direction of the reactor tubes; (III) the catalytic particle radius; and (IV) the time. However, when the research focuses principally on investigating the possibility to implement high time-computing CAPE (Computer-Aided Process Engineering) solutions such as nonlinear model predictive control, real-time dynamic optimization, and reactor hot-spot monitoring, the mathematical model is usually satisfactory to characterize the process transients if its axial behaviour and the time evolution are well-simulated. Moreover, according to Table 1, it is possible to completely characterize the methanol synthesis reactor through the definition of mass balances only for two compounds, water and methanol, being the mass fraction of the remaining species directly dependent on them: in fact, the rank of compounds/elements matrix is $r = 3$ and two mass balance equations are enough to completely characterize the system.

*Table 1: Compound-element matrix for the methanol synthesis*

| | **CO** | **$CO_2$** | **$H_2$** | **$CH_3OH$** | **$H_2O$** |
|---|---|---|---|---|---|
| ***C*** | 1 | 1 | 0 | 1 | 0 |
| ***O*** | 1 | 2 | 0 | 1 | 1 |
| ***H*** | 0 | 0 | 2 | 4 | 2 |

It is not superfluous to remark that, as highlighted elsewhere (Manenti *et al.*, 2011), even though the methanol yield is particularly small, there is a significant deviation in the numerical results if the molar decrease across the reactor is neglected. Hence, the following two independent balances for methanol and water are reported in mass fractions by definition:

- Methanol:

$$\varepsilon_b \rho_{gas} \frac{\partial \omega_{CH_3OH}}{\partial t} = -\frac{M}{A_{\text{int}}} \frac{\partial \omega_{CH_3OH}}{\partial z} + \mathrm{D}\rho_g \frac{\partial^2 \omega_{CH_3OH}}{\partial z^2} + MW_{CH_3OH} r_{CH_3OH} \tag{1}$$

- Water:

$$\varepsilon_b \rho_{gas} \frac{\partial \omega_{H_2O}}{\partial t} = -\frac{M}{A_{\text{int}}} \frac{\partial \omega_{H_2O}}{\partial z} + \mathrm{D}\rho_g \frac{\partial^2 \omega_{H_2O}}{\partial z^2} + MW_{H_2O} r_{H_2O} \tag{2}$$

The energy balance results in:

$$\begin{aligned} &\left[\varepsilon_b \rho_{gas} c_{p_{mix}} + \left(1-\varepsilon_b\right)\rho_{cat} c_{p_{cat}}\right]\frac{\partial T}{\partial t} = \\ &\quad = -\frac{M}{A_{\text{int}}} c_{p_{mix}} \frac{\partial T}{\partial z} + \pi \frac{U}{A_{\text{int}}}\left(T_{shell} - T\right) + \left[r_{CH_3OH}\left(-\Delta H_{r_1}\right) + r_{H_2O}\left(-\Delta H_{r_2}\right)\right] \end{aligned} \tag{3}$$

where:

$$r_{CH_3OH} = \rho_{cat}(1-\varepsilon_b)\eta_1(r_{CO\rightarrow CH_3OH} + r_{WGS}) \quad (4)$$

$$r_{H_2O} = \rho_{cat}(1-\varepsilon_b)\eta_2(r_{CO_2\rightarrow CH_3OH} + r_{WGS}) \quad (5)$$

## 3. Numerical Strategy

The method of lines is adopted for the numerical integration (Ozisik, 1994; Ullmann's, 2007). To prevent numerical discontinuities it is suitable to express the derivatives in their central form. By doing so, the system cannot be integrated node by node, rather its overall structure is considered as the dependencies of the $n-th$ node deal with both $(n-1)-th$ and $(n+1)-th$ nodes. The resulting Jacobian matrix assumes the diagonal-block-band structure of Figure 1.

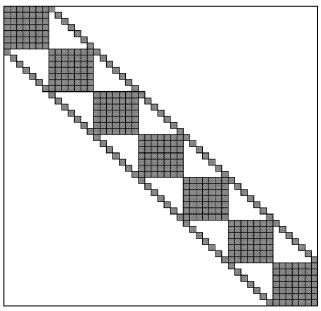

*Figure 1: Jacobian qualitative structure. The number of blocks depends on the discretization across the reactor axis.*

Such a structure entails the simultaneous solution of all nodes for each time interval (Buzzi-Ferraris and Manenti, 2010). The class *BzzOdeSparseStiff* in BzzMath library (Buzzi-Ferraris, 2010) is adopted for its capability to exploit the matrix sparsity and the system structure so as to ensure fast computational times in spite of the complexity of the system we are solving. We investigated both the parabolic and the hyperbolic PDE system by noting superior performances of the parabolic model: (I) it avoids non-physical oscillations generated by a first-order system; (II) the convection term can be approximated by using a forward formulation, leading to a more stable simulation; (III) more realistic solutions are obtained, since thermal diffusion term is significantly relevant in this particular system: the high conductivity of the copper solid catalyst supports thermal diffusion along the reactor axis, impacting therefore the kinetics of reactions. For the sake of conciseness, we report parabolic model results only in the dedicated section.

### 3.1 Adaptive Grids

After having opportunely coupled a detailed mathematical model for the methanol synthesis reactor with the most appropriate numerical methods to solve the resulting PDE system, the adaptive grids are also implemented to make the discretization denser where required (Figure 2) and sparser elsewhere. It is suitable to have a denser

discretization in correspondence with the hot spot position so as to improve the estimation accuracy; thus a static upgrade is carried out to have more points in correspondence with the first 2 m of the reactor, whereas the grid is made sparser in the remaining 5 m in order to preserve the total amount of nodes and therefore to preserve the computational effort required to solve the system. By doing so, a better accuracy is obtained around the hot spot position in spite of the final part of the reactor, where process dynamics are less relevant than the ones occurring in the first 2 m.

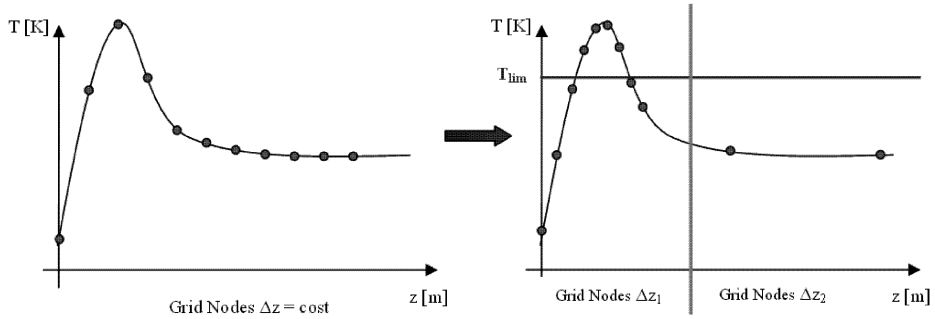


*Figure 2: Qualitative scheme of adaptive grids aimed at making the profile characterization denser in correspondence with the temperature hot-spot.*

## 4. Results

As stated above, the parabolic formulation of the PDE system leads to a diagonal-block-band matrix; the introduction of the diffusive term (second order derivatives) allows to remove the non-physical oscillations generated by solving numerically the hyperbolic system (first order derivatives); in addition, it allows to approximate the convective term using a forward formulation (stable with respect to the backward formulation) to obtain a more realistic solution. Figure 3 shows the profile of methanol mass fraction across the reactor. At $t = 0[s]$ the steady-state operating conditions are perturbed by a step-disturbance on the shell-side temperature: from the steady-state value of 523°C to 500°C. The perturbation propagates as expected along the reactor and the process dynamics is completely developed in one minute. Note that at lower temperatures the methanol conversion is practically halved. No other trends are reported for the sake of conciseness. Last but not least, the step disturbance here assumed is intentionally hard in order to measure the computational effort under high dynamics regime. It is remarkable the computational time reduction obtained by introducing the diffusive term and moving from a first order to a second order PDE system (Table 2). The reason is the same as mentioned above: the diffusive term allows to stabilize the system reducing non-physical oscillations. Very efficient differential solvers (Manenti et al., 2009b) allow to take benefit of matrix sparsity and structure, contributing to computational time reduction in a determining way, especially looking forward the implementation of nonlinear model predictive control methodology.

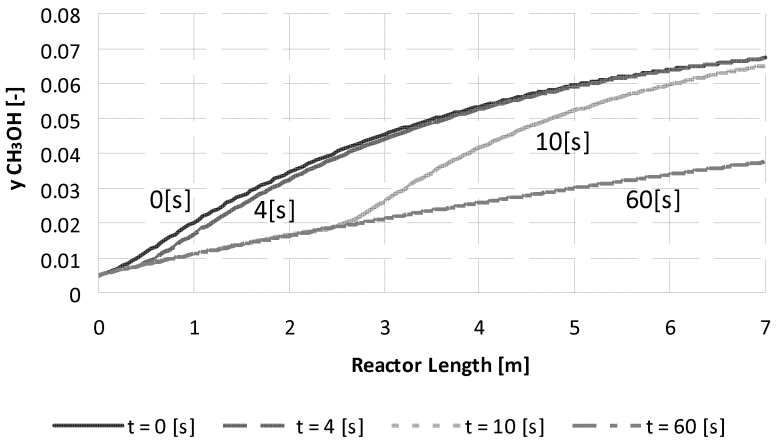


*Figure 3: Methanol mass fraction profile across the reactor under a step-perturbation (at time t=0[s]) of the shell side temperature (523°C to 500°C).*

*Table 2: CPU times to simulate 100s under the same perturbation of Figure 3; System: Intel® Core2™ Quad, 2.85 GHz, 3.0 GB RAM; Windows XP™ SP3; Visual Studio 6.0.*

| | |
|---|---|
| *First order derivatives* | 78.02 s |
| *Second Order derivatives* | 36.23 s |

## 5. Conclusions

A reasonably detailed dynamic model for the Lurgi-type shell and tube boiler-reactor for methanol synthesis has been described. An investigation on the most appealing numerical methods has been performed, showing that a good efficiency is obtained in the numerical integration of the parabolic formulation of the model. This formulation takes advantage of the resulting diagonal-blocks-band structure of the Jacobian: despite of an increase in problem dimensionality, the matrix sparsity and structure have been both exploited efficiently by the implementation of ad hoc solvers. The reduced computational effort gives the possibility to study the implementation of the nonlinear model predictive control methodology on the Lurgi-type configuration.

## Nomenclature

| | | | | | |
|---|---|---|---|---|---|
| $A_{\text{int}}$ | Internal area of the tube | $[m^2]$ | M | Mass flowrate | $\left[\frac{kg}{s \cdot tube}\right]$ |
| $a_v$ | Specific surface area of the catalytic pellet | $\left[\frac{m^2_{cat}}{m^3_{cat}}\right]$ | $MW_i$ | Molar weight of i-th component | $\left[\frac{kg_i}{kmol_i}\right]$ |
| $c_{p_{mix}}$ | Specific heat of gas at constant pressure | $\left[\frac{J}{kg \cdot K}\right]$ | $T$ | Temperature of the gas phase | $[K]$ |

| | | |
|---|---|---|
| $T_{shell}$ | Temperature of the shell-side of reactor | $[K]$ |
| U | Overall heat transfer coefficient | $\left[\frac{W}{m^2 \cdot K}\right]$ |
| Z | Axial coordinate | $[m]$ |
| $r_{WGS}$ | Reaction rate Water Gas Shift | $\left[\frac{mol}{s \cdot kg_{cat}}\right]$ |
| $r_{CO \to CH_3OH}$ | Reaction rate of methanol from carbon monoxide | $\left[\frac{mol}{s \cdot kg_{cat}}\right]$ |
| $r_{CO_2 \to CH_3OH}$ | Reaction rate of methanol from carbon dioxide | $\left[\frac{mol}{s \cdot kg_{cat}}\right]$ |
| $\varepsilon_b$ | Void fraction of catalytic bed | $[-]$ |
| $\Delta H_j^{reac}$ | Enthalpy of j-th reaction | $\left[\frac{J}{mol}\right]$ |
| $\eta_j$ | Efficiency of Reaction j-th | $[-]$ |
| $\rho_{cat}$ | Density of the catalytic pellet | $\left[\frac{kg_{cat}}{m^3_{cat}}\right]$ |
| $\rho_{gas}$ | Density of the gas phase | $\left[\frac{kg}{m^3}\right]$ |
| $\omega_{\text{i}}$ | Mass fraction of component i in the gas phase | $[-]$ |

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