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Model Predictive Control for Hydrogen Production in a Membrane Methane Steam Reforming Reactor

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The main aim of this study is the design of an optimal model predictive controller (MPC) scheme for the control of a fixed-bed membrane reactor (MR) for H_2 production via low temperature methane steam reforming (MSR). Reactions take place over a Ni-Pt/CeZnLa foam supported catalyst at an operating temperature of 773 K and pressure of 10^6 Pa. A permeable membrane with Pd-Ru deposited on a ceramic dense support is used to selectively remove the produced H_2 from the reaction zone. In this way, the separated H_2 is free of CO_2 and CO, whereas chemical equilibrium is shifted favourably towards H_2 production, thus enabling the achievement of a high CH_4 conversion at relatively low temperature levels. A rigorous nonlinear dynamic model has been developed assuming one dimensional transport and pseudo-homogenous conditions in the reaction zone in order to emulate the plant dynamics, whereas a linearized version of it is employed for the MPC algorithm. Simulated case studies of the control scheme on the nonlinear system confirm the controller ability to achieve the desired dynamic behaviour both in the case of H_2 production changes and disturbance compensation.

1. Introduction

Methane steam reforming is a conventional method to produce synthesis gas from hydrocarbon fuels. The produced synthesis gas can be used in Fisher-Tropsch and other processes for highly valuable products (De Falco et al., 2011). Otherwise, hydrogen can be separated from synthesis gas and can be used in applications such as fuel cells for clean energy production. The use of a membrane reactor in methane reforming equipped with a Pd based membrane that utilizes its extremely high selectivity towards hydrogen, is an alternative for enhanced efficiency of the overall process. High methane conversion can then be achieved at a much lower reactor temperature than in conventional methane steam reforming reactors, as the removal of hydrogen from the reaction zone through the membrane shifts the chemical equilibrium towards hydrogen production (Kyriakides et al., 2014). The membrane makes the reactor highly interactive since heat, material, and reaction rates must be well balanced in order to maintain the optimal operating conditions. Since several factors may disturb the operation of the reactor, the design and implementation of an efficient control system is quite important. The present work aims to develop a model predictive controller that can exploit the predictive properties of the reactor model to compensate for the disturbances affecting the process system.
Despite a large number of studies that provide insights regarding the optimal operating conditions of methane steam reforming in a membrane reactor, only a very limited number of works focus on describing the complex dynamic interactions that occur inside such a reactor. Sheintuch et al. (2011) investigated the optimal conditions for an autothermal packed-bed membrane reformer. Kyriakides et al. (2015) calculated through a systematic optimization scheme the optimal steam to carbon ratio and sweep gas flow rate that minimize the overall methane. Wu et al. (2015) presented a stand-alone syngas production process (steam methane

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reforming and dry reforming in a traditional reactor) and proposed a multi-loop control system to ensure low CO_2 emissions. The optimization-based control configuration for a low temperature ethanol steam reformer for hydrogen production in a traditional reactor aiming at obtaining the desired flow of hydrogen while keeping carbon monoxide at its nominal operating level under constraints was presented by Recio-Garrido et al. (2012). Koch et al. (2013) presented the static and dynamic characteristics of an ethanol membrane reformer and the implementation of an efficient controller to reduce the response time of the reformer. Mikhalevich et al. (2015) developed a control system based on PID (proportional-integral-derivative) feedback loops. The literature survey demonstrates that the systematic design of efficient control systems for membrane methane steam reforming reactors needs further investigation. This work attempts to address the control issues in such reactor systems using model predictive control methods.

2. Process description, reaction scheme and kinetic model

The main control objective is to satisfy the desired high hydrogen production rate in a low temperature membrane methane steam reforming reactor while maintaining the produced hydrogen stream free of CO and CO_2 and thus operating efficiently. The membrane reactor consists of two coaxial tubes as shown in Figure 1a. The area between the two tubes defines the reaction zone, whereas the area inside the inner tube, which is consisted of a Pd-Ru layer deposited on a ceramic dense support, forms the permeation zone. A mixture of CH_4 and steam is fed into the reaction zone that surrounds the membrane at a defined molar steam to carbon ratio. MSR and water-gas shift (WGS) reactions take place over the Ni-Pt/CeZnLa foam supported catalyst at a temperature range of 723 - 823 K and at a reaction pressure of 10 bar (Angeli et al., 2013). The difference between the square roots of H_2 partial pressure in the reaction and in permeation zones is the driving force for H_2 removal through the selectively permeable Pd-Ru membrane. A sweep gas stream, usually a N_2 or steam, that flows through the permeation zone carries the permeated hydrogen to storage and ensures a high driving force for hydrogen separation. The length of the reaction zone is 0.5 m, whereas the length of the membrane is 0.4 m attached on a draft tube used for support. The pilot plant design is motivated by a large industrial system, where heat is supplied by molten salts that exploit energy from solar troughs, where maximum operating temperature must be less than 823 K (Giaconia et al., 2013). A detailed description of the experimental unit can be found at Kyriakides et al. (2016).

Figure 1: (a) Membrane reactor for low temperature MSR and (b) MPC closed loop block diagram.

The reaction scheme shown in Table 1, involves two reversible reactions, one endothermic (MSR) and one exothermic (WGS). The reaction rate expressions are based on the Langmuir-Hinselwood mechanism given by Xu and Froment (1989).

Table 1: Reaction scheme of the membrane steam reforming

Reaction		Reaction Enthalpy
Methane steam reforming	$CH_4+H_2O \leftrightarrow CO+3H_2$	ΔH^o_{298}=206,000 J/mol
Water-Gas swift	$CO+H_2O \leftrightarrow CO_2+H_2$	ΔH^o_{298}=-41,000 J/mol
Overall Methane steam reforming	$CH_4+2H_2O \leftrightarrow CO_2+4H_2$	ΔH^o_{298}=165,000 J/mol

3. Mathematical Modelling

3.1 Membrane reactor

The model predictive control scheme requires the use of an accurate and reliable process model. A linear process model is preferable as the dynamic optimization problem which is solved at every control interval would require significantly less computational effort than a nonlinear model. The linear process model for

control purposes is derived by linearization of a nonlinear dynamic process model developed for the reactor system. The nonlinear model is a pseudo-homogeneous, one-dimensional (axial direction) that consists of: a) the mass balances for every component in both the reaction, Eq(1), and permeation zones, Eq(2), b) the energy balance in the reaction zone, Eq(3), and c) the momentum balance in both the reaction and permeation zone, Eq(4). H_2 flux through the membrane is calculated by Sieverts law, Eq(5).

$$\frac{\partial C_i}{\partial t} = -u\frac{\partial C_i}{\partial z} + \rho_b \sum_{j=1}^{3} R_j v_{i,j}, \quad i = CH_4, H_2O, CO, CO_2$$
$$\frac{\partial C_i}{\partial t} = -u\frac{\partial C_i}{\partial z} + \rho_b \sum_{j=1}^{3} R_j v_{i,j} - \frac{2r_i}{r_o^2 - r_i^2} N_m, \quad i = H_2 \tag{1}$$

$$\frac{\partial C_{i,p}}{\partial t} = -u_p \frac{\partial C_{i,p}}{\partial z} + \frac{2}{r_i} N_m, \quad i = H_2, \quad \frac{\partial C_{i,p}}{\partial t} = -u_p \frac{\partial C_{i,p}}{\partial z}, \quad i = N_2 \tag{2}$$

$$\rho C_p \frac{\partial T}{\partial t} = -u\rho C_p \frac{\partial T}{\partial z} + \rho_b \sum_{j=1}^{3} \Delta H r_j R_j + \frac{2r_o}{r_o^2 - r_i^2} h_w (T_w - T) \tag{3}$$

$$\frac{\partial(\rho u)}{\partial t} + \frac{\partial(\rho u^2)}{\partial z} = 0 \qquad \frac{\partial(\rho_p u_p)}{\partial t} + \frac{\partial(\rho_p u_p^2)}{\partial z} = 0 \tag{4}$$

$$N_m = \frac{Q \exp(-E/R_g T_m)}{d_m} \left(P_{H_2,r}^{0.5} - P_{H_2,p}^{0.5}\right) \tag{5}$$

The main model assumptions are as follows: a) plug-flow conditions implying that backmixing effects are considered negligible, b) ideal-gas behaviour, as reactor pressure was low to moderate, c) 100 % selectivity of the membrane towards H_2; therefore, permeation of other components is negligible, d) pseudo-homogeneous model; the catalytic bed and reacting mixture are considered as a homogeneous medium with uniform properties, e) radial gradients in reaction and permeation zone are negligible, f) constant temperature and pressure in the permeation zone at their inlet values, g) heat exchange between permeation and reaction zones is negligible, and h) constant wall temperature in the reactor heating jacket is considered. The boundary conditions in the reaction zone for the wall and membrane side, as well as at the reactor inlet are given below:

$$z = 0 \ : \ C_i = C_{i,in}, \quad i = CH_4, H_2O, H_2, CO, CO_2, \quad u = u_{in}, \quad T = T_{in}, \quad P = P_{in}$$
$$C_{j,p} = C_{j,p,in}, \quad j = N_2, H_2, \quad u_p = u_{p,in} \tag{6}$$

Modelling equations Eq(1-6) have been discretized using a backward finite differencing. The number of selected grid points in the axial direction is Nz = 30 and are equally spaced. The model includes 300 differential equations and 310 variables. Ten variables, which correspond to the inlet stream conditions (concentration, temperature, and pressure) and wall temperature, are fixed. The nonlinear model is linearized around the desired operating conditions for use in the model predictive control scheme.

3.2 Model Predictive Control

The aim of model predictive controller is to calculate a sequence of actions for the manipulated variables in the system that satisfies a performance index. The performance index includes the desired trajectory for the process system and the effort of the manipulated variables over a prediction horizon extending into the future. Then, at each control interval, only the first of the calculated control actions is applied to the system. At the end of each control interval, new measurements for the state variables are acquired and the initial point for the linearized model is updated accordingly. The entire calculation is repeated for the next interval but with the prediction horizon shifted by one control interval. The MPC is formulated in the state space form, as described by Wang (2009), where the process system is described by a linear discrete time dynamic model, such as:

$$x_m(k+1) = A_m x_m(k) + B_m u(k)$$
$$y(k) = C_m x_m(k) \tag{7}$$

where, *u(k)* is the manipulated variables vector, *y(k)* the controlled variables vector and $x_m(k)$ is the state vector. Taking a difference operation on Eq(7), we obtain that:

$$x_m(k+1) - x_m(k) = A_m\big(x_m(k) - x_m(k-1)\big) + B_m\big(u(k) - u(k-1)\big) \tag{8}$$

And by the use of incremental notation (*Δ*), we obtain:

$$\Delta x_m(k+1) = A_m \Delta x_m(k) + B_m \Delta u(k) \tag{9}$$

If we choose a new state variable vector such as $x(k) = [\Delta x_m(k); \quad y(k)]$, and knowing that:

$$y_m(k+1) - y_m(k) = C_m\big(x_m(k+1) - x_m(k)\big) = C_m \Delta x_m(k+1) = C_m\big(A_m \Delta x_m(k) + B_m \Delta u(k)\big) \tag{10}$$

An augmented state space model is obtained:

$$\overbrace{\begin{bmatrix}\Delta x_m(k+1)\\ y(k+1)\end{bmatrix}}^{x(k+1)} = \overbrace{\begin{bmatrix}A_m & 0_m\\ C_m A_m & 1\end{bmatrix}}^{A}\overbrace{\begin{bmatrix}\Delta x_m(k)\\ y(k)\end{bmatrix}}^{x(k)} + \overbrace{\begin{bmatrix}B_m\\ C_m B_m\end{bmatrix}}^{B}\Delta u_m(k)$$
$$y(k) = \overbrace{[0_m \quad 1]}^{C}\overbrace{\begin{bmatrix}\Delta x_m(k)\\ y(k)\end{bmatrix}}^{x(k)} \tag{11}$$

in order for the change of control action (*Δu*) to be used in the objective function instead of the control action (*u*) itself. Such formulation is necessary for zero steady-state error. Given the augmented state space model, the future control actions vector *Δu(k)* can be obtained by the solution of a quadratic optimization problem:

$$\min_{\Delta U} J = \min_{\Delta U}\left(\sum_{i=1}^{Np}\Big(y_{sp}(k+i) - y(k+i)\Big)^T Q\Big(y_{sp}(k+i) - y(k+i)\Big) + \sum_{i=1}^{Nc}\Delta u(k+i-1)^T R \Delta u(k+i-1)\right) \tag{12}$$

subject to:

$$\Delta u^{min} \le \Delta u \le \Delta u^{max} \qquad u^{min} \le u(k) \le u^{max} \qquad y^{min} \le y(k) \le y^{max} \tag{13}$$

Where y_{sp} is the output set-point, $Np = 40$ is the length of the prediction horizon, $Nc = 20$ is the length of the control horizon and $Q = 1$ and $R = [1\ u(2)/u(1)\ u(3)/u(1)\ u(4)/u(1)]$ are weight matrices of the output and the rate of change of the input variables. Symbols $u(1) - u(4)$ denote the nominal steady state values of the manipulated variables, namely CH_4, H_2O, and sweep gas flow rates and wall temperature, Weight matrix R is formed in such way that all input's effect in cost function is properly scaled and of the same order of magnitude. Also the time (control) interval is set equal to $Ts = 30$ s.

The developed MPC is designed to maintain the hydrogen production rate at the desired level and uses as manipulated variables methane, steam and sweep gas inlet flowrates and wall temperature (assumed that can be controlled indirectly through the flow of the heating medium). Constraints are established in both the manipulated variable, to denote the physical bounds of the actuators, and in the rate of change for the manipulated variables, to limit sharp and aggressive response of the control system.

Figure 1b shows the block diagram of the closed loop MPC system. The actual plant is emulated using the nonlinear process model of Eq(1-6), whereas the model block refers to the linearized model around a known system's operating point as described in Table 2. The state variables update block involves a single integrating disturbance model that enforces in the future state predictions the difference between the linear model prediction and the plant output over the entire prediction horizon. The integrating disturbance model along with the objective function in the MPC that incorporates the rate of change for the manipulated variables, *Δu*, introduces integral action in the controller and guarantees zero steady-state offset.

Table 2: System's operating point

Variable	Value	Variable	Value
Methane inlet flowrate	4.16*10^{-6} [m^3/s]	Wall heat transfer coefficient	100 [J/(K mol)]
Steam to Carbon ratio	3 [~]	Membrane thickness (Pd based layer)	5*10^{-6} [m]
Reaction zone inlet temperature	773 [K]	Pre-exponential coefficient (Sieverts Law)	3.77*10^{-8} [mol/(Pa$^{0.5}$ms)]
Reaction zone inlet pressure	1.013*10^6 [Pa]	Activation energy (Sieverts Law)	15700 [J/mol]
Reactor's length	0.5 [m]	Sweep gas inlet flowrate	4.16*10^{-6} [m^3/s]
Membrane diameter	0.014 [m]	Permeation zone inlet temperature	773 [K]
Reactor's diameter	0.04125 [m]	Permeation zone inlet pressure	1.013*10^5 [Pa]
Wall temperature	773 [K]		

4. Simulation Results

The developed MPC is tested for its ability to achieve the desired dynamic behaviour for both setpoint changes and disturbance rejection scenarios. The imposed setpoint trajectory on pure H_2 production is shown in Figure 3(a) (dashed lines). The disturbance scenario involves a series of step changes in the pre-exponential factor of the Sieverts law (Figure 3(b)) that implies the deactivation of the palladium membrane, possibly due to competitive absorption. The two scenarios are performed in the membrane reactor system simultaneously.

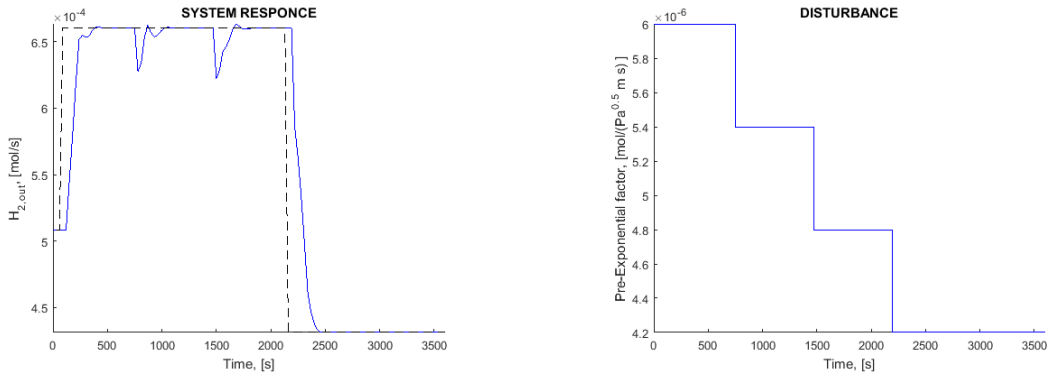

Figure 3: (a) Pure hydrogen production (controlled variable) and setpoint trajectory, (b) Imposed disturbance scenario on measurable pure H_2 production flowrate.

The dynamic behaviour of the controller shows (Figure 3(a)) that the tracking of the setpoints and the disturbance rejection is satisfactory. The small deviations from the setpoint level occur at the time instances that the disturbances are imposed. A quick recovery of the production level is achieved despite the quite severe change in the membrane permeability. The compensation has been achieved with proper adjustment of the steam to carbon ratio and the reactor wall temperature as shown in Figure 4.

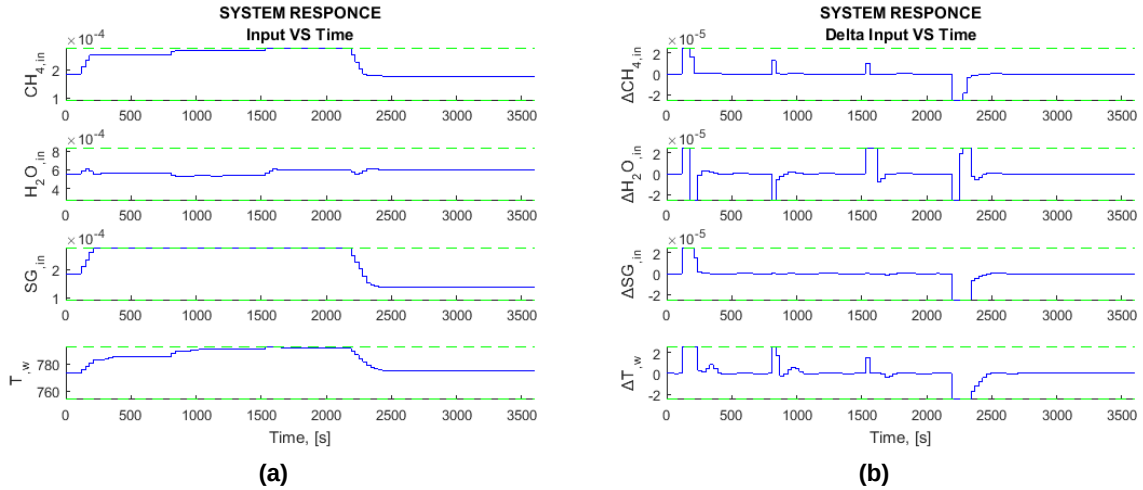

Figure 4: (a) Input (Methane, Steam, Sweep Gas and Wall Temperature) manipulation over time, (b) change of control variable over time.

The imposed constrains on the manipulated variables and on the rate of change of the manipulated variables (Figure 4) are depicted with the green dashed line. Flowrates bounds (methane, steam and sweep gas, respectively) are set to ± 50 %, whereas wall temperature bound is set to ± 2.5 % of the nominal operating point. Respectively, the range for the manipulated variable rate of change is set to ± 2.5 (× 10^{-5} mol/s for flowrate and K for wall temperature).

5. Conclusions

A rigorous mathematical model for the simulation and control of a Pd-Ru membrane reactor where low temperature methane steam reforming takes place for hydrogen production was presented in this study. An advanced model predictive control strategy that calculated the optimal sequence of the manipulated variables over a specified control horizon has been implemented in order to achieve the desired dynamic behaviour both in the case of desired reference point change and disturbance compensation scenarios. While small deviations occurring at the time instances that the disturbances are imposed, a quick recovery of the production level is achieved, despite the quite severe change in the membrane permeability. Results referring to the dynamic behaviour of pure hydrogen production are satisfactory, based on this outcome, the next step should be the development of a control framework aiming to the maintenance of process control targets while minimizing fuel consumption and maximizing hydrogen separation.

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