On-Line Estimation of Inlet and Outlet Composition in Catalytic Partial Oxidation

Ali Al-Matouq, Tyrone Vincent

Department of Electrical Engineering and Computer Science, Colorado School of Mines 1600 Illinois St., Golden, CO 80401, USA

Abstract

An estimation strategy is presented for determining inlet and outlet composition of catalytic partial oxidation (CPOX) of methane over rhodium catalyst using simple, fast measurements: temperature, and thermal conductivity. A 1-D high fidelity simulation model for CPOX studied in [1] for a portable fuel cell application is developed and enhanced for transient experiments. Process dynamics are analysed to demonstrate how solid temperatures along the axes of the reactor reflect the endothermic/exothermic interplay of reactions during a process upset. Model reduction is then used to obtain a low complexity model suitable for use in a moving horizon estimator with update rates faster than 0.02 seconds. System theoretic observability analysis is then conducted to predict the suitability of different measurement designs and the best locations for temperature measurements for estimating both inlet and outlet gas mole fractions for all species. Finally, a Moving Horizon estimator is implemented and simulation experiments are conducted to verify the accuracy of the estimator.

Keywords: Catalytic Partial Oxidation, Moving Horizon Estimation, Descriptor Systems

1. Introduction

Catalytic partial oxidation reforming of methane is an efficient process used to produce syngas (H2 and CO) using a fuel mixture that contains methane CH4 and oxygen O2. CPOX reforming is a compact size low-capital cost reactor that is suitable for portable applications as in fuel cells. CPOX is also being considered as a potential process for large scale production of syngas in view of its economic and environmental advantages over steam reforming [2].

Fast and accurate measurement of both inlet and outlet gas mole fractions is essential for process reliability and to effectively maintain the quality specifications on syngas. Fuel cells, for example, require varying inlet H2 concentrations in the stack depending on load demands while maintaining low CO content to avoid poisoning the cell. Furthermore, polymer electrolyte membrane (PEM) fuel cells require low CO2 concentrations. Restrictions on H2O content can also be present. Different fuel cell and fuel processing control strategies can make use of accurate measurements of species mole fractions of the gas coming in and out from the CPOX reactor to enable feed-forward temperature control of the reactor, prevent excess H2 generation, prevent fuel cell stack starvation and/or prevent CPOX clogging [3], [4].

In this paper an estimator for inferring both inlet and outlet gas mole fractions in real time is developed. The developed state estimator can be used in portable fuel cell applications for monitoring and/or control. It can also be used in case the main composition measurement device is off-line and a substitute is needed to enhance reliability. The estimator design uses a single output measurement, such as thermal conductivity or gas density, that is combined with temperature measurements along the reactor and nominal input flows. In order to obtain well defined input and output composition estimates, these measurements are reconciled against a reactor model using a moving horizon estimator.
Previous work towards the development of a nonlinear observer for the CPOX process was given in [5]. A simple lumped parameter model was used that relied on one temperature measurement and one gas species composition measurement at the outlet to infer the remaining outlet gas species compositions at the outlet. The model used, however, was based on only two global reactions; partial and total oxidation and did not account for steam and dry reforming reactions. Further work in [6] was made for estimating inlet gas CH$_4$/O$_2$ ratio in the context of biogas reforming. Also, a simple lumped parameter model of a continually stirred reactor model was used but combined with a detailed reaction mechanism. In both models, spatial variations in temperature along the reactor were not accounted for, not to mention other important mass and energy transport effects present in the CPOX reforming process.

This paper is an extension of these two studies in multiple directions. First, a high fidelity 1-D model for CPOX process, originally studied in [1] and experimentally verified in [7], is developed and enhanced for transient simulation experiments. The high fidelity model captures the possible transport and kinetic effects in the lateral direction, assuming homogeneity in the radial and angle coordinates. A detailed analysis of process dynamics is conducted to determine the important measurements suitable for state estimation. The analysis revealed that solid temperatures across the reactor foam monolith have different dynamics and are highly correlated with the disturbances in the C/O ratio of the inlet gas. The different temperature dynamics are associated with the exothermic/endothermic interplay of reactions along the reactor.

Second, several transient simulation experiments with random variations in the inlet C/O ratio were conducted. The collected simulation data was then used to fit a high order state space model using linear subspace identification techniques [8]. The resulting high order state space model is then reduced in size using balanced truncation with matched DC gain. The state space model is then transformed into a descriptor model that is suitable for unknown input estimation and can incorporate the consistency condition in which the sum of mass fractions in the outlet gas stream must equal to one. A descriptor system observability analysis is performed to evaluate different measurement designs that guarantee numerical stability and uniqueness of the estimates. Local observability analysis of the low complexity model indicated that three temperature measurements spread apart combined with either a density or thermal conductivity measurement of the outlet gas stream allows a well conditioned and stable estimator to be designed.

Third, a moving horizon state estimator that incorporates the low complexity descriptor model, best measurement design, known inequality constraints of the CPOX process is then developed. State estimator performance in terms of mean square error is then verified via simulation. The estimation accuracy, in terms of mean square error values, was in the order of $O(10^{-5})$ with very good performance for inlet gas O$_2$, CH$_4$ and outlet gas H$_2$, CO and Ar species mole fractions and marginal accuracy for other variables due to unaccounted non-linearities.

The linearized system identification/model reduction strategy used in this study provided solution times of less then 0.02 seconds per iteration which are adequate for the CPOX process time scales but with some compromise in estimation accuracy. Another advantage is that no quasi-steady state assumptions were needed and the time scales of the original high fidelity model are retained in the low complexity model. Finally, the solution strategy is implementable on a stand alone microprocessor using custom C code generated from CVXGEN available in [9] which can speed implementation even further.

The organization of the paper is as follows: Section 2 will present the detail model equations of the CPOX reactor used in this study. Section 3 will describe the efforts used to accelerate transient simulations of the model followed by an analysis of process dynamics. Section 4 will discuss the process of extracting a low complexity model using subspace identification techniques combined with model reduction. Section 5 will formulate the desired state estimation problem to be solved by forming a descriptor model of the process followed by local observability analysis for different proposed measurement designs. Section 6 will present the Moving Horizon State Estimator algorithm for descriptor systems that will be used and finally Section 7 will present the results obtained followed by a discussion in Section 8.

2. Model Description

The CPOX reformer model adapted in this work was developed in [1] and was also validated via experiments in [7] in the context of biogas fuel reforming. The system consists of a reactor tube made from a catalyst-loaded Al$_2$O$_3$ ceramic foam installed inside a furnace as depicted in Figure 1. Feed flows of CH$_4$, O$_2$, and Ar are metered with
mass-flow controllers and mixed prior to entering a temperature-controlled tube furnace. The model incorporates a
detailed reaction mechanism for methane oxidation over Rhodium using the mechanism studied in [10] and a dusty
gas model for transport in $\alpha\ Al_2O_3$ foam monoliths. A brief review of the model equations and parameters as given in
[1] will be presented first for the convenience of the reader since this model will be used in the subsequent simulation
experiments.

2.1. Model Equations

The equations for each grid in the 1-D model is first presented. The nomenclature and units used in this study
is summarized in Table 1 for the key variables. The species and mass continuity equations in conservative form are
given as:

$$\phi_g \frac{\partial \rho_g Y_i}{\partial t} + \nabla \cdot j_i = (\phi_g \omega_i + A_s \delta_i) W_i, \quad i = 1, \ldots, K_g$$

(1)

$$\phi_g \frac{\partial \rho_g}{\partial t} + \sum_{i=1}^{K_g} \nabla \cdot j_i = \sum_{i=1}^{K_g} A_s \delta_i W_i$$

(2)

where $\rho_g$ is the gas phase density, $\phi_g$ is foam porosity, $Y_i$ is the mass fraction for species $i$ in the gas phase, $j_i$ is
the mass flux for species $i$, $\omega_i(T_g)$ and $\delta_i(T_s)$ are the homogeneous and heterogeneous reaction rates evaluated at gas
and surface temperatures respectively, $W_i$ is the molecular weight for species $i$, $A_s$ is the specific surface area of the
active catalysts (i.e. active surface area per unit volume of foam) and $K_g$ is the number of gas phase species. Since
the residence time of the reactor is smaller than the gas phase reaction rates, it is possible to neglect the gas phase
reactions; i.e. $\omega_i \approx 0$. In the equations, $\nabla$ is used to denote differentiation with respect to the space variable. The mass
density can be determined by the ideal equation of state as follows:

$$\rho_g = \frac{p}{RT_g \sum_{i=1}^{K_g} \frac{\rho_g Y_i}{W_i}}$$

(3)

where $p$ is the gas pressure. The mass fluxes $j_i$ are determined using the Dusty-Gas model from the following implicit
relationship:

$$\sum_{l \neq k} \left[ \frac{[X_l]}{[X_l]} \frac{\partial}{\partial l} \right] J_{kl} + \frac{J_l}{D_{k,Kn}} = -\nabla [X_l] - \frac{[X_l]}{D_{k,Kn}} - \frac{B_{lg}}{\mu} \nabla$$

(4)

where $J_l$ is the molar flux of gas phase $i$, $[X_i]$ is the molar concentration for gas species $i$, $[X_T] = p/RT$ is the total
molar concentration of the gas, and $B_{lg}$ is the permeability which may be found for example using the Kozeny-Carman

Figure 1: Process Flow Diagram
The energy balance equations for both the gas phase and the solid phase are respectively given as follows:

\[ \frac{\partial \rho_g e}{\partial t} + \nabla \mathbf{q}_g = -q_{\text{conv}} - q_{\text{surf}} \]  

(6)

\[ \frac{\partial \rho_s}{\partial t} (\rho_s c_{ps} T_s) + \nabla \mathbf{q}_s = q_{\text{conv}} + q_{\text{surf}} - q_{\text{env}} \]  

(7)

where \( \phi_s = 1 - \phi_g \) is the solid phase volume fraction, \( T_s \) is the solid temperature, \( \rho_s \) is the solid phase density, \( c_{ps} \) is the heat capacity of the solid phase at constant pressure, and \( \mathbf{q}_g, \mathbf{q}_s, q_{\text{conv}}, q_{\text{surf}}, q_{\text{env}} \) are respectively the heat flux within the gas phase, heat flux within the solid phase, heat flux due to convection between the gas and solid phase, heat flux due to surface reactions between the gas and solid phase, and heat flux due to radiation between the solid phase and the environment. Finally \( e \) is the gas internal energy which can be expressed as \( e = \sum_{i=1}^{n} \gamma_i e_i \). In differential

Table 1: Model Nomenclature and Units

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_g )</td>
<td>gas phase density</td>
<td>kg.m(^{-3} )</td>
</tr>
<tr>
<td>( Y_i )</td>
<td>Mass fraction for species ( i )</td>
<td></td>
</tr>
<tr>
<td>( w_i )</td>
<td>homogeneous reaction rate</td>
<td>mole.m(^{-3} )s(^{-1} )</td>
</tr>
<tr>
<td>( s_i )</td>
<td>heterogeneous reaction rate</td>
<td>mole.m(^{-3} )s(^{-1} )</td>
</tr>
<tr>
<td>( W_i )</td>
<td>Molecular weight of species ( i )</td>
<td>kg/mole</td>
</tr>
<tr>
<td>( p )</td>
<td>Gas pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>( j_i )</td>
<td>mass flux for gas species ( i )</td>
<td>kg.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( J_i )</td>
<td>molar flux for gas species ( i )</td>
<td>mole.m(^{-3} )s(^{-1} )</td>
</tr>
<tr>
<td>( [X_i] )</td>
<td>molar concentration for gas species ( i )</td>
<td>mole.m(^{-3} )</td>
</tr>
<tr>
<td>( T_s )</td>
<td>Solid phase temperature</td>
<td>K</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Gas phase temperature</td>
<td>K</td>
</tr>
<tr>
<td>( q_g )</td>
<td>Heat flux within the gas phase</td>
<td>J.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( q_s )</td>
<td>Heat flux within the solid phase</td>
<td>J.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( q_{\text{conv}} )</td>
<td>Heat flux due to convection</td>
<td>J.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( q_{\text{surf}} )</td>
<td>Heat flux due to surface reactions</td>
<td>J.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( q_{\text{env}} )</td>
<td>Heat flux due to radiation</td>
<td>J.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( e )</td>
<td>Gas internal energy</td>
<td>J.kg(^{-1} )</td>
</tr>
<tr>
<td>( c_{pi} )</td>
<td>Specific heat capacity at constant pressure for species ( i )</td>
<td>J.kg(^{-1} )K(^{-1} )</td>
</tr>
<tr>
<td>( h_i )</td>
<td>Specific gas enthalpy for species ( i )</td>
<td>J.kg(^{-1} )</td>
</tr>
<tr>
<td>( A_{gk}, A_s )</td>
<td>Gas mixture and solid phase thermal conductivity</td>
<td>J.m(^{-1} )s(^{-1} )K(^{-1} )</td>
</tr>
<tr>
<td>( h_v )</td>
<td>Volumetric heat transfer coefficient</td>
<td>W.m(^{-3} )K(^{-1} )</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Gas mixture viscosity</td>
<td>kg.m(^{-1} )s(^{-1} )</td>
</tr>
<tr>
<td>( m_g )</td>
<td>Total gas mass flux</td>
<td>kg.m(^{-2} )s(^{-1} )</td>
</tr>
<tr>
<td>( \theta_i )</td>
<td>Surface site coverage for species ( i )</td>
<td></td>
</tr>
</tbody>
</table>
form \(\frac{de}{dt} = \sum_{i=1}^{K_s} Y_i c_{v,i} dT_g\) where \(c_{v,i}\) is the specific heat capacity at constant volume for gas species \(i\). Hence, the chain rule may be used to rewrite (6) as:

\[
\phi_g \sum_{i=1}^{K_s} \rho_g Y_i c_{v,i} \frac{\partial T_g}{\partial t} + \nabla q_s = -\phi_g \sum_{i=1}^{K_s} \rho_g Y_i \frac{\partial T_g}{\partial t} e_i - \dot{q}_{conv} - \dot{q}_{surf}
\]

This modified implementation of equation (6) can make use of (1) which simplifies integration.

The gas and solid phase heat fluxes \(q_g, q_s\) are given as:

\[
q_g = -\phi_g \lambda_g \nabla T_g + \sum_{i=1}^{K_s} h_i \dot{j}_i, \quad (8)
\]

\[
q_s = -\lambda_s' \nabla T_s, \quad (9)
\]

where \(h_i\) are the species specific enthalpy and \(\lambda_g\) is gas mixture thermal conductivity; see [12] for mixing rule used, and \(\lambda_s'\) is the temperature dependent effective conductivity of the solid phase given by:

\[
\lambda_s' = \phi_s \lambda_s + \lambda_r
\]

where \(\lambda_s\) is the thermal conductivity of the solid and \(\lambda_r\) is the effective radiation conductivity (due to optically thick porous foam) is found from the following empirical formula [1]:

\[
\lambda_r = 4d_p \sigma T_s^3 \left[ 0.5756 \epsilon \tan^{-1} \left( 1.5353 \lambda_s' \frac{0.8011}{\epsilon} \right) + 0.1843 \right]
\]

where \(\lambda_s' = \lambda_s / (4d_p \sigma T_s^3)\), \(\sigma\) is the Stefan-Boltzmann constant, \(d_p\) is an effective particle diameter and \(\epsilon\) is the emissivity of the solid material.

The convection heat flux \(\dot{q}_{conv}\) is given by:

\[
\dot{q}_{conv} = h_v (T_g - T_s) \quad (10)
\]

where \(h_v = A_{conv} h\) is the volumetric heat transfer coefficient, where \(h\) is the conventional heat transfer coefficient and \(A_{conv}\) is the specific surface area of the porous foam. The value of \(h_v\) can be obtained from the Nusslet number correlation referenced in [1] as:

\[
Nu = \frac{h_v d_e^2}{\lambda_g} = 2.0 + 1.1 Re^{0.6} Pr^{1/3}
\]

where \(d_e\) is the mean catalyst particle diameter, \(Re = \rho d_e v / \mu\) is the Reynolds number based on the total gas mass flux \(\dot{m}_g = \sum_{i=1}^{K_s} j_i\) and \(Pr\) is the Prandtl number given in Table 2.

The net heat release rate resulting from heterogeneous surface reactions \(\dot{q}_{surf}\) is the enthalpy flux rates of gas-phase species to and from the catalyst surface:

\[
\dot{q}_{surf} = -A_s \sum_{i < 0} \dot{j}_i W_i h_i(T_g) - A_s \sum_{i \geq 0} \dot{j}_i W_i h_i(T_s) \quad (11)
\]

where the convention \(\dot{j}_i < 0\) indicates a net gas species flux from the gas toward the surface and vice versa. The symbol \(h_i(T_g)\) denotes enthalpies of the gas phase species evaluated at the gas phase temperature and \(h_i(T_s)\) denotes enthalpies of the gas phase species evaluated at the solid phase temperature. Note that \(\dot{q}_{surf}\) was subtracted from (6) as opposed to being added as a source term in (7) due to sign convention.

The radiative heat flux from the foam to the surroundings is given as:

\[
\dot{q}_{env} = \sigma \epsilon A_{env} (T_s - T_\infty) \quad (12)
\]
<table>
<thead>
<tr>
<th>Para.</th>
<th>Value</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>2.54 × 10⁻²</td>
<td>Reactor length</td>
<td>m</td>
</tr>
<tr>
<td>τ</td>
<td>2</td>
<td>Tortuosity of foam monolith</td>
<td></td>
</tr>
<tr>
<td>φ_f</td>
<td>0.75</td>
<td>Porosity of foam monolith</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2.52 × 10⁻¹₃</td>
<td>Permeability of foam</td>
<td></td>
</tr>
<tr>
<td>r_p</td>
<td>280 × 10⁻⁶</td>
<td>Average pore radius</td>
<td>m</td>
</tr>
<tr>
<td>d_p</td>
<td>850 × 10⁻⁶</td>
<td>Particle diameter of foam</td>
<td>m</td>
</tr>
<tr>
<td>ε</td>
<td>0.5</td>
<td>Emissivity of quartz</td>
<td></td>
</tr>
<tr>
<td>A_env</td>
<td>337</td>
<td>Interface area of reactor</td>
<td>m²</td>
</tr>
<tr>
<td>A_s</td>
<td>1.4</td>
<td>Quartz Conductivity</td>
<td>W.m⁻¹.K⁻¹</td>
</tr>
<tr>
<td>A_x</td>
<td>40,000</td>
<td>Catalyst surface area</td>
<td>m⁻¹</td>
</tr>
<tr>
<td>D</td>
<td>1.3 × 10⁻²</td>
<td>Diameter of the reactor tube</td>
<td>m</td>
</tr>
<tr>
<td>v</td>
<td>3.5</td>
<td>Inlet gas velocity</td>
<td>m.s⁻¹</td>
</tr>
<tr>
<td>ρ_s</td>
<td>3970</td>
<td>Density of quartz</td>
<td>kg m⁻³</td>
</tr>
<tr>
<td>c_p,s</td>
<td>1225</td>
<td>Specific heat of quartz</td>
<td>J.kg⁻¹.K⁻¹</td>
</tr>
<tr>
<td>T</td>
<td>2.6 × 10⁻⁹</td>
<td>Active catalyst site density</td>
<td>mole.cm⁻²</td>
</tr>
<tr>
<td>T_in</td>
<td>1023</td>
<td>Inlet gas temperature</td>
<td>K</td>
</tr>
<tr>
<td>T_so</td>
<td>1073</td>
<td>Furnace temperature</td>
<td>K</td>
</tr>
<tr>
<td>T_w</td>
<td>1073</td>
<td>Initial wall temperature</td>
<td>K</td>
</tr>
<tr>
<td>X_1</td>
<td>12.4, 6.2, 81.4</td>
<td>Inlet gas mole fraction</td>
<td>%CH₄, %O₂, %Ar</td>
</tr>
<tr>
<td>P_in</td>
<td>1</td>
<td>Inlet gas pressure</td>
<td>atm</td>
</tr>
<tr>
<td>P_out</td>
<td>0.9996</td>
<td>Outlet gas pressure</td>
<td>atm</td>
</tr>
<tr>
<td>P_r</td>
<td>0.7</td>
<td>Prandtl number</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Model parameters

where $A_{env}$ is the interface area of the porous foam and $T_{so}$ is the surrounding environment temperature of the furnace.

The site coverages of surface species $\theta_i$ can be obtained from the following balance equation:

$$\frac{d\theta_i}{dt} = \frac{\dot{\xi}_i}{\Gamma}, \quad i = 1, \cdots, K_s$$

(13)

where $\Gamma$ is the density of the active catalyst sites on the total surface area of the foam monolith and $K_s$ is the total number of surface species. The consistency conditions in the model are as follows:

$$\sum_{i=1}^{K_s} Y_i = 1, \quad \sum_{i=1}^{K_s} \theta_i = 1$$

(14)

The equality constraint for the mass fractions is already embedded in (1) and is shown here to be used later. The reaction rates are calculated internally within Cantera [12] using the reaction mechanism given in [10] which contains 42 elementary reactions, 7 gas species (H₂, O₂, H₂O, CH₄, CO, CO₂, AR) and 12 surface species (Rh(s), H(s), H₂O(s), OH(s), CO(s), CO₂(s), CH₄(s), CH₂(s), CH₃(s), CH₄(s), C(s), O(s)). Moreover, Cantera was used to find the densities, heat capacities, enthalpies, conductivities and viscosities for the gas phase. Details of these calculations can be found in Cantera documentation available online. Table 2 gives the dimensions and parameters used in the study.

3. Model Simulation and Process Dynamics

3.1. Model Simulation

The partial differential algebraic system of equations are stiff; i.e. the associated dynamics exhibit both very short time scales, due to fast heterogeneous reactions, and very long time scales due to heat transfer dynamics. For
steady state simulation the boundary conditions of the model were: constant inlet mass flow rate (set by specifying the inlet velocity \( v_{\text{in}} \) and inlet mass fractions \( Y_{\text{i}} \)), constant inlet gas temperature \( T_{\text{In}} \), constant furnace temperature \( T_{\infty} \) and constant outlet temperature and pressure of the gas phase, \( T_{\text{Out}} \) and \( P_{\text{Out}} \) respectively. Figure 2 shows a simplified diagram with the variables being discussed.

The model is one dimensional; i.e. it captures spatial variation in the z-direction only. The system of equations was discretized in space using second order approximation for the spatial derivatives. A non-uniform mesh was designed using a logarithmic function with more grids concentrated in the first 0.5 cm of the reactor. The thermodynamic and kinetic calculations were calculated using Matlab Cantera [12]. The combined model equations was then integrated using Matlab’s stiff integrator “ode15s” [13] using a relative error tolerance of \( 1 \times 10^{-4} \) and an absolute error tolerance of \( 1 \times 10^{-6} \). An effort was made to speed up transient simulations by calculating a compressed numerical Jacobian matrix that exploits sparsity and also by code profiling. Mole fractions are shown in the developed plots instead of mass fractions for practicality purposes. Figure 3 shows the mole fraction (top) and the solid temperature profiles along the axes of the reactor at steady state using a non-uniform mesh with 10 grids. These steady state results are comparable with the results given in [1] for the base line case defined by the values given in Table 2.

3.2. Process Dynamics

Transient analysis of start up conditions was given in [14], where the dynamics of total oxidation, partial oxidation and steam reforming, and their interplay in the different sections of the reactor was studied. Here, the overall dynamics of the process when the inlet gas feed is subject to step changes in oxygen and methane during normal operation is analysed. The overall reactions that compete with each other in the CPOX process are the exothermic partial oxidation, endothermic steam reforming, endothermic dry reforming and exothermic combustion reactions that are globally and respectively expressed as follows:

\[
\begin{align*}
\text{CH}_4 + \frac{1}{2} \text{O}_2 & \rightarrow \text{CO} + 2 \text{H}_2, \quad \Delta H_R = -36 \text{ kJ/mol} \\
\text{CH}_4 + \text{H}_2\text{O} & \leftrightarrow \text{CO} + 3 \text{H}_2, \quad \Delta H_R = +206 \text{ kJ/mol} \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2 \text{CO} + 2 \text{H}_2, \quad \Delta H_R = +247 \text{ kJ/mol} \\
\text{CH}_4 + 2 \text{O}_2 & \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}, \quad \Delta H_R = -802 \text{ kJ/mol}
\end{align*}
\]

In the simulation study, the feed composition is a mixture of \( \text{CH}_4, \text{O}_2 \) and \( \text{Ar} \) only. Figures 4 and 5 depict a transient simulation experiment where 3 step changes were made to the \( \text{O}_2 \) and \( \text{CH}_4 \) mole fractions. Figure 4 shows the inlet perturbations (top) and the resulting time response of the solid temperatures across the reactor. Figure 5 shows the response of the mole fractions in both the entry and the exit sections of the reactor.

The step changes at \( t = 1 \) sec cause a sudden increase in the \( \text{CH}_4/\text{O}_2 \) ratio from 2 to 2.31 in the inlet gas stream. The associated solid temperature dynamics show a drop in temperatures at the entry portion of the reactor (in the first 0.23 cm portion measured from the entry) and a slight increase in temperatures at the remaining portion of the reactor.
reactor (from 0.23 cm to 2.54 cm). The trajectories for the gas mole fractions in Figure 5 (top) show an increase in $\text{H}_2$ and CO content and a drop in $\text{H}_2\text{O}$ content at the reactor entry associated with this step change. On the other hand, the dynamics near the exit portion of the reactor, also shown in Figure 5 (bottom), shows only a slight increase in $\text{H}_2$, CO and $\text{H}_2\text{O}$ content of the gas, but also less $\text{CH}_4$ conversion. This suggests that endothermic steam reforming reactions start to increase at the entry portion of the reactor due to the increase in $\text{CH}_4$/H$_2$O ratio (from 1.25 to 1.73) producing more $\text{H}_2$ and CO. This excess CO, however, will cause more carbon to deposit on the catalyst active sites downstream to form C(s). This can be confirmed by examining Figure 6 which shows the trajectories of the species surface coverages. This in turn will free some H$_2$O and O$_2$ generated by surface reactions that will then react with the excess $\text{CH}_4$ exothermically downstream. Hence, the increase in $\text{CH}_4$/O$_2$ ratio from 2 to 2.31 resulted in an unfavourable condition due to less conversion of $\text{CH}_4$ and partially deactivating the catalyst.

The step changes at $t = 11$ sec shows a more drastic increase in the $\text{CH}_4$/O$_2$ ratio from 2.31 to 3.13 in the inlet gas stream. The associated solid temperature and mole fraction dynamics suggest an increase in both steam reforming and dry reforming reactions at the entry portion of the reactor. However, near the reactor exit, the transient plots reflect a sharp drop in $\text{CH}_4$ conversion, which is expected since severe catalyst deactivation has occurred at this stage as reflected in Figure 6.

The step changes at $t = 21$ sec shows a decrease in the $\text{CH}_4$/O$_2$ ratio from 3.13 to 1.6 in the inlet gas stream. The associated solid temperature and mole fraction dynamics suggest the opposite of the previous scenario; an increase in exothermic reactions across the reactor, with a slight increase in endothermic reactions near the exit. At this stage, the catalyst has been reactivated by freeing active sites from C(s) and forming CO and CO$_2$, as suggested in Figures 5.
Figure 4: Transient simulation experiment: Inlet gas step changes (top) and associated solid temperature dynamics (bottom)

and 6.

The above analysis suggests that solid temperature measurements across the reactor can be an indispensable measurement for inferring the inlet gas disturbances and the associated outlet gas mole fractions using the model.

4. Model Simplification and Reduction

4.1. Method Justification

As demonstrated previously in Section 3, the dynamics of gas compositions, surface coverages and temperatures exhibit different time scales. The residence time of the process is in the order of ~ 0.01 seconds which further complicates the implementation of real time optimization routines. Moreover, the target application of the CPOX reformer is a portable fuel cell that has cost constraints on the amount of processing power available. Hence, it is important to find a real time estimation solution strategy that can provide reasonable estimates of gas compositions appropriate with the time scales and cost constraints of the process.

The full discritization embedded optimization strategy used in [15], for example, implemented a Moving Horizon Non-linear Programming estimator for a chemical reacting flow problem with 300-400 ODEs which is comparable in size to the CPOX model being used in this study (which consist of 348 ODEs). The quasi-steady state assumption on the reaction kinetics in [15] was used to resolve model stiffness and the method required full discritization using orthogonal collocation on finite elements for the time variable and Euler approximation on the distance variable. In addition, availability of explicit Jacobian and Hessian model equations and an interior point solver with sparsity information was needed to reduce problem complexity. Solution times obtained using this strategy, however, ranged from 8.7 seconds to 188 seconds on a personnel computer (depending on the horizon length selected for the Moving Horizon Estimator). The same strategy was also used in [16] for a less complex model with solution times of 30
Figure 5: Transient simulation experiment: associated dynamics for the first grid (top) and the last grid (bottom) for gas mole fractions.
seconds on average using a horizon length of 10 for a control problem. Based on these results, this solution strategy was not used for the CPOX process application in view of the model complexity of the CPOX process, the time constraints and implementability restrictions.

Another different approach was used in [17] for a slow distillation column process that used a multiple shooting strategy which involved integration of the model in every optimization step. The solution times obtained per iteration using Moving Horizon Estimation was ~ 4 seconds on average. The method, however, relies on the availability of a simulation model that can be integrated rapidly using large time steps, which is possible for process models that do not exhibit stiffness.

Hence, a different solution strategy was used that can be implemented on stand-alone microprocessors and can provide solution times relevant to the CPOX process time scales with some compromise in estimation performance. The strategy relies on using system identification techniques as a means for simplifying the model while retaining the predictive capabilities of the full order model. The simplified model is then utilized in fast convex state estimation algorithms that are implementable on stand-alone microprocessors using custom developed library free C code [9]. No quasi-steady state assumptions were used in the high fidelity model in order to capture the time scales accurately in the reduced model and to make use of the detail reaction mechanism model. This model simplification strategy, even though localized to a single operating point, can be extended to multiple operating points using a linear parameter varying model as discussed for example in [18]. The accelerated transient simulation model developed in Section 3 permits conducting long experiments required to obtain a linearised model with acceptable accuracy.

4.2. Subspace Identification

A series of transient simulation experiments were conducted to collect a large set of input/output data at a sample rate of 0.001 seconds. The inlet methane and oxygen mass fractions were varied using a normally distributed pseudo-random number generator [13], with mean zero and variance of 0.006 added to the nominal mass fractions; 0.0544 ±0.006 and 0.0545±0.006 (i.e. about 10% variation). Figure 7 shows a portion of the transient simulation experiments that were conducted.

The desired input and output variables grouped in vectors \( u_k, y_k \) respectively are defined as follows:

\[
\begin{align*}
    y_k^T & := [T_{s,k}^1, T_{s,k}^2, \ldots, T_{s,k}^{l'}, Y_{in,CH_4}^k, Y_{in,O_2}^k, Y_{Out,H_2}^k, Y_{Out,H_2O}^k, Y_{Out,CO}^k, Y_{Out,CO_2}^k, Y_{Out,AR}^k] \\
    u_k^T & := [Y_{in,CH_4}^k, Y_{in,O_2}^k] 
\end{align*}
\]

(15)

(16)

where \( T_{s,k}^l \) is the solid temperature of the tube reactor at the \( lth \) grid at time period \( k \), \( Y_{Out,H_2}^k \) is the mass fraction of H\(_2\) in the outlet gas at time period \( k \). Similarly, \( Y_{Out,O_2}^k, Y_{Out,CH_4}^k \) are mass fractions of O\(_2\) and CH\(_4\) in the inlet gas at time period \( k \) respectively. This selection was based on the state estimator problem design considerations which will be discussed.
later in this study. However, models for other variables in the system; i.e. the internal gas densities $\rho_g$, the surface coverages $\theta_i$, the gas temperatures $T_g$ etc., can be developed using the same methodology presented if desired.

The mean values of the collected input and output data $\bar{u}, \bar{y}$ was found and subtracted from $u_k, y_k$ respectively. The de-averaged data was then used in the system identification subspace algorithm N4SID studied in [8]. The linear state space model to be identified and reduced is of the form:

$$x_{k+1} = Ax_k + Bu_k$$
$$\hat{y}_k = Cx_k + Du_k$$ (17a)

where $\hat{y}_k = y_k - \bar{y}, \hat{u}_k = u_k - \bar{u}$ and $x_k \in \mathbb{R}^n$ is the state vector sequence that has no physical meaning. The subspace identification problem is defined as: given a set of input/output vector sequences $(\hat{u}_k, \hat{y}_k)$, for $k = 1, \cdots, T$, estimate the order of the system $n$ and the system matrices $A, B, C, D$ up to a similarity transform of the state vector sequence $\tilde{x}_k = T^{-1}x_k$.

The general steps for subspace identification are discussed here briefly: [19]

1. Regression/Projection: A least squares regression or projection is performed to estimate one or several high order-models. This step entails forming the input and output Hankel matrices and a projection operator to find a least squares approximation of the observability matrix.
2. Model Reduction: The high order model is then reduced to an appropriate low dimensional subspace that is observable. This can be achieved using singular value decomposition of the observability matrix with different pre-weighting techniques to reduce the effect of noise. The canonical variance analysis, studied in [20] was used in this study.
3. Parameter Estimation (Realization): The reduced order observability matrix is then used to estimate the matrices $A, B, C, D$ which are unique up to a similarity transform of the state vector $x_k$. This can be achieved using matrix decompositions or least squares minimization methods.

For more details on the assumptions required on the system for open loop sub-space identification and the detail algorithm the reader is referred to [19].

Separate high order discrete state space models were identified for each individual output; i.e. for each variable in $\hat{y}_k$. The sample rate was 0.1 seconds. Canonical variate analysis pre-weighting of the observability matrix was used [20]. This resulted in 18 linear state space models that were combined to form one model by stacking together the system matrices for the individual models obtained. The resulting model had 18 outputs, 2 inputs and 784 states; i.e. $n = 784$. To limit the measurement bandwidth, the model was re-sampled so that 1 sec measurements can be used assuming zero-order hold on the input $u_k$ as follows:

$$x_{k+10} = A^{10}x_k + [A^9B + A^8B + \cdots + B]u_k$$
$$y_k = Cx_k + Du_k, \quad u_k = u_{k+1} \cdots = u_{k+10}$$

4.3. Model Reduction

Model reduction was then performed on this high order linear state space model using balanced truncation with matched DC gain that discards the states with small Hankel singular values while preserving the DC gain of the original model [21]. The model order was reduced from 784 to 7 states by observing the number of dominant singular values and the minimum model order that preserves input/output behaviour. Figure 7 shows a comparison between the simulation of the output resulting from this reduced linear model and the output obtained from simulating the original high fidelity model for both solid temperatures and outlet gas thermo-conductivity. From the shown results, the reduced order linear model exhibits very good performance in the operating region under study, which is sufficient for the purpose.

5. Problem Formulation and Observability Analysis

5.1. Problem Formulation

Before defining the state estimation problem, some essential variable definitions are first presented. The output data vector $y_k$ given in (15) can be split into two vectors: vector of desired outputs to be estimated $y^T_{out,k}$ and the
Figure 7: Comparison between reduced order linear model (dashed line) and original first principle model (hard line) for solid temperature profile and outlet gas thermoconductivity vs. time

The known operating point $\bar{y}$ is also split as $\bar{y} = [\bar{y}_{\text{out}}, \bar{y}_{\text{meas}}]$ according to (18a) and (18b). A noisy detrended measurement $\tilde{y}_{\text{meas},k}$ is defined as follows:

$$\tilde{y}_{\text{meas},k} := y_{\text{meas},k} - \bar{y}_{\text{meas}} + v_k$$

where $v_k$ represents measurement noise that is assumed to be normally distributed iid random sequence with 0 mean and covariance matrix $R$; i.e. $v_k \sim N(0, R)$. An augmented state vector is defined as:

$$x_k^T = [x_k^T \tilde{u}_k^T]$$

Equation (17b) can be used to write an equation for $y_{\text{out},k}$ as follows:

$$y_{\text{out},k} = [C_{\text{out}} D_{\text{out}}]x_k + \tilde{y}_{\text{out}}$$

where $C_{\text{out}}, D_{\text{out}}$ are the rows of $C$ and $D$ associated with $y_{\text{out},k}$ respectively and $\tilde{y}_{\text{out}}$ is the known mean value of the outlet mass fractions extracted from $\bar{y}$. Note: $\bar{y}, \tilde{u}$ are given from the system identification step explained before and depend on the operating point.
It is desired to design the state estimator such that it can account for possible unmeasured inlet disturbances to the process. Possible inlet disturbances can be fluctuations in the inlet gas mass fractions, inlet gas temperature and environment temperature. All possible disturbances, including disturbances arising from parameter uncertainty, will be modelled using a normally distributed iid random sequence \( w_k \sim N(0, Q) \) added to (17a) that is independent from \( v_k \). The resulting stochastic linear model of the process and noisy measurements are given as follows:

\[
\begin{bmatrix}
I & -B \\
A & 0
\end{bmatrix} x_{k+1} = 
\begin{bmatrix}
A & 0 \\
C_{\text{meas}} & D_{\text{meas}}
\end{bmatrix} x_k + w_k + v_k 
\]

\( y_{\text{meas},k} = 
\begin{bmatrix}
C_{\text{meas}} & D_{\text{meas}}
\end{bmatrix} x_k + v_k 
\)

The matrices \( C_{\text{meas}}, D_{\text{meas}} \) are the rows of \( C \) and \( D \) associated with \( y_{\text{meas},k} \) respectively. The stochastic model composed of (21a) and (21b) is called a stochastic linear descriptor system \([22]\).

It is desired to incorporate the known consistency relationship (14) as an additional deterministic measurement to (21b) by making use of (20) as follows:

\[
0 = 1 - I^T \tilde{y}_{\text{out}} = I^T [C_{\text{out}} D_{\text{out}}] x_k
\]

where \( I^T \) is a vector of ones that effectively acts as a summation operator, \( y_{\text{out},k}^d \) is a deterministic measurement which is a constant and \( C_{\text{out}} \) is the deterministic measurement matrix. Both (21b) and (22) can be combined in one equation by forming an augmented measurement vector \( y_k \) and the resulting process and measurement model will become as follows:

\[
E x_{k+1} = Ax_k + w_k 
\]

\[
y_k = H x_k + v_k
\]

where:

\[
y_k = 
\begin{bmatrix}
y_{\text{meas},k} \\
y_{\text{out},k}^d
\end{bmatrix},
H = 
\begin{bmatrix}
C_{\text{meas}} \\
C_{\text{out}}
\end{bmatrix},
v_k = 
\begin{bmatrix}
v_k \\
0
\end{bmatrix},
w_k = w_k
\]

Consequently, if an estimate of the augmented state vector \( x_k \) is found, an estimate for both \( u_k \) and \( y_{\text{out},k} \) using the known operating points \( \bar{u}, \bar{y} \) and (20) can also be found. Hence, the state estimation problem can now be formally stated as follows: Given the measurement vector \( y_k \) for \( k = 0, 1, \cdots, t \), an a priori estimate of the initial state as a random variable \( x_0 \sim N(x_0, P_0) \) and the stochastic/deterministic model (23a) and (23b) find an estimate of the augmented state vector sequence \( x_k \) for \( k = 0, 1, \cdots, t \).

### 5.2. Observability Analysis for the Reduced CPOX Process Model

Observability analysis of descriptor systems of the general form (for both square and rectangular systems) was studied in \([23]\) using a special Kalman decomposition derived using geometric analysis. Observability ensures that \( x_k \) can be found in finite time if the corresponding values of \( w_k, y_k \) are known and the solution is unique (assuming \( v_k = 0 \)). In the context of state estimation, where \( w_k, v_k \) are unknown random sequences that may or may not be zero, system observability ensures convergence to unique unbiased estimates of \( x_k \). \([22]\) The following is a useful tool to determine observability.

**Theorem 5.1.** (Descriptor System Kalman Decomposition \([23]\))

Let \( E, A \in \mathbb{R}^{n \times n_1} \), where \( n < n_1 \) and \( H \in \mathbb{R}^{n \times n} \), then there exists non-singular transformation matrices \( P \in \mathbb{R}^{n \times n} \) and \( Q \in \mathbb{R}^{n_1 \times n_1} \) such that:

\[
(PEQ \cdot PAQ \cdot HQ) = 
\begin{bmatrix}
E_{11} & E_{12} \\
0 & E_{22}
\end{bmatrix},
\begin{bmatrix}
A_{11} & A_{12} \\
0 & A_{22}
\end{bmatrix},
\begin{bmatrix}
0 & H_2
\end{bmatrix}
\]
and the corresponding noise free system becomes:

\[
\begin{bmatrix}
E_{11} & E_{12} \\
0 & E_{22}
\end{bmatrix}
\begin{bmatrix}
x_{k+1}^{o} \\
x_{k+1}^{no}
\end{bmatrix}
=
\begin{bmatrix}
A_{11} & A_{12} \\
0 & A_{22}
\end{bmatrix}
\begin{bmatrix}
x_{k}^{o} \\
x_{k}^{no}
\end{bmatrix}
\]

\[
y_{k} =
\begin{bmatrix}
0 & H_{2}
\end{bmatrix}
\begin{bmatrix}
x_{k}^{o} \\
x_{k}^{no}
\end{bmatrix}
\]

where the transformation:

\[
Q^{-1}x_{k} =
\begin{bmatrix}
x_{k}^{o} \\
x_{k}^{no}
\end{bmatrix}
\]

separates the observable states \(x_{k}^{o}\) from the un-observable states \(x_{k}^{no}\).

This theorem can be used to examine observability as follows. The Kalman decomposition of the simplified model of the process and measurements given by \((E, A, H)\) is first found by calculating the required transformation matrices \(P\) and \(Q\) using an implementation of the geometric technique given in [23]. The decomposition \((PEQ, PAQ, HQ)\) is then calculated and verification of \(E_{11} = A_{11} = 0\) and \(E_{12} = A_{12} = 0\) is done to examine whether all states are observable. A software for Kalman filter decomposition for non-square descriptor systems was developed which can be downloaded from [24]. Following these steps, the following observations were made:

1. If a thermo-conductivity measurement is not used at the outlet gas stream, a minimum of 3 spatially separated temperature measurements are required to ensure observability.
2. If only a thermo-conductivity measurement of the outlet gas stream is used, than the system is not observable.
3. The system is observable if one temperature measurement and one thermo-conductivity measurement is used. However, the temperature measurement must be installed at the entrance of the reactor.

These observations agree with the intuition that outlet gas thermal-conductivity alone can not uniquely determine composition since multiple mixtures of gas can have the same thermo-conductivity. Moreover, temperature sensitivity to inlet gas disturbances is highest at the entrance of the reactor, which is very evident from Figure 5. Estimator performance and the extent of observability will be examined by finding the steady state error covariance values of the estimates in Section 7. It is worth mentioning that having an observable linearised reduced model does not imply "global" observability of the original model, however, the intention for conducting observability analysis in this section was to obtain a healthy estimator design.

6. Moving Horizon Estimation Algorithm for Descriptor Systems

The Kalman state estimation algorithm for descriptor systems given in [25] is now briefly presented, which can accommodate models described by mixed stochastic and deterministic equations. The maximum likelihood/maximum a posterior objective function to be minimized to find an optimal estimate for \(x_{k}\) was given as:

\[
J(x_{k}) = \frac{1}{2}(||E_{x_{1}} - A_{x_{0}}||_{P_{k+1}}^{2} + \sum_{k=1}^{T-1}||w_{k}||_{Q}^{2} + \sum_{k=0}^{T-1}||v_{k}||_{R}^{2}),
\]

subject to (23a) and (23b)

where \(P_{0} = Q + AP_{0}A^{T}\) and the decision variables for minimization are the unknown state vectors \(x_{1}, x_{2}, \cdots, x_{T}\). To simplify notation, the quadratic form symbol \(||z||_{A}^{2} = z^{T}A^{-1}z\) was used.

A recursive solution to this objective function was derived in [25] and can be implemented to solve the state estimation problem presented earlier in real time. However, it is desired to introduce additional prior knowledge in the form of known linear inequality constraints on the state vector \(x_{k}\) as follows:

\[
Fx_{k} \leq d
\]
For example, it is known that mass fractions must be a number in the range [0, 1]. Also, it may be known that the input mass fraction of methane can not exceed a positive number $c < 1$. These constraints, and other similar ones, can be represented by (25) by appropriately specifying the matrix $F$ and vector $d$. This additional prior knowledge can be very effective in increasing the accuracy of the state estimator [26] [27]. The absence of this information, on the other hand, can introduce significant errors when the system is operating near the constraints, as demonstrated in [28].

However, if (25) is imposed in the minimization problem (24), a recursive solution to the problem can not be obtained any more. This is because these inequality constraints must be satisfied at all times and the decision variables in the optimization problem will grow unbounded with $t$. Moving horizon estimation, MHE, first introduced in [29] for linear state space systems, is a technique to approximately solve the constrained optimization problem (24) and (25) by minimizing over a fixed window in time of size $N$ and ignoring all the cost terms outside this window. An extra cost term is added to the objective function that serves to account for the ignored information outside the window. Hence, the size of the minimization problem is fixed and can be solved in real time using quadratic programming algorithms. The constrained moving horizon state estimator problem at the current time $k = t$ enables us to estimate $x_k$ for $k = t-N, \cdots , t$ and can be stated as follows:

$$
\tilde{p}_{k}^{mh} = \min_{(x_k)_{k=N}^t} \Gamma_{t,N}^{mh}(x_{t-N}) + \sum_{k=t-N}^{t-1} ||w_k||_{Q}^2 + \sum_{k=t-N}^{t-1} ||v_k||_{R}^2 \\
\text{subject to } Fx_k \leq d, (23a), (23b)
$$

(26)

Here, $N$ is the length of the horizon of the moving horizon state estimator which defines the size of the window in past that the state estimator explicitly accounts for, $\Gamma_{t,N}^{mh}(x_{t-N})$ is an extra cost term, which is a function of $x_{t-N}$, selected by the designer and only used at times $k > N$. In loose terms, this extra cost term should be selected such that its minimization will effectively summarize the knowledge of the ignored data in the past before time $k = t - N$ on the state estimates at times $k = t - N, \cdots , t$. [30]

The significance of the cost term $\Gamma_{t-N}^{mh}(x_{t-N})$ on the stability of the optimal state estimator is emphasized in [31] and [30] for linear discrete time state space systems. This cost term was related to the arrival cost known in dynamic programming. Using dynamic programming an analytical expression for the arrival cost for the unconstrained minimization problem (24) can be derived. Consequently, this arrival cost can be used as the extra cost term in (26) which approximates the true arrival cost. Moreover, this selection of $\Gamma_{t-N}^{mh}(x_{t-N})$ guarantees stability of the Moving Horizon state estimator. The arrival cost for the unconstrained problem (24) can be derived using the matrix identities presented in [25] and is given by:

$$
\Gamma_{t-N}^{mh}(x_{t-N}) = \frac{1}{2} ||E x_{t-N} - A x_{t-N}^{mh}||_{P_{t-N}}^2 + J_{t-N-1}
$$

(27)

where $x_{t-N}^{mh}$ is the optimal estimate obtained from solving the minimization problem (26) at time $k = t - N - 1$ and $J_{t-N-1}$ is the cost of minimizing the unconstrained function (24) which is a number that has no influence on the solution. Moreover, $P_{t-N}$ is calculated from the Kalman filter recursions [25] that account for equity constraints arising from deterministic equations. Algorithm I summarizes the technique used to find the Moving Horizon state estimate that was applied to the CPOX estimation problem in Section 7. Note, Ker(M) denotes the kernel of matrix M which is an orthobasis spanning the null space of matrix M. The reader is referred to [25] to understand the basis for these calculations.

7. Results and Discussion

A new transient simulation experiment was conducted to collect data to test the estimator discussed in the previous section. Random perturbations of magnitude 13% of nominal values were added to the nominal values of oxygen and methane mass fractions; i.e. $0.0544 \pm 0.0007$ and $0.0545 \pm 0.0007$ respectively. In addition, random white noise was added to these signals with mean zero and variance 0.005. Three solid temperature measurements positioned at 0.13 cm, 0.57 cm and 2.54 cm from the reactor entrance was used. Also a thermo-conductivity measurement installed at the reactor outlet, as suggested in the previous observability analysis, was included as a measurement. Random white noise was added to the measurements obtained from simulation with variance of $5$ for solid temperatures and 0.0001
Algorithm 1: Moving Horizon Estimation

Input Data:

\[ \mathbf{E}, \mathbf{A}, \mathbf{C}_{\text{meas}}^{d}, \mathbf{C}_{\text{meas}}^{i}, \mathbf{P}_0, \mathbf{Q}, \mathbf{R}, \mathbf{y}_k, \mathbf{\hat{x}}_0, \mathbf{\hat{y}}_0, \mathbf{\hat{u}} \]

Initializations:

\[ \mathbf{M} = \text{Ker}(\mathbf{C}_{\text{meas}}^{d}), \quad p_k^{(\ast)} = P_0, \quad k = 1 \]

Minimization Problem:

\[ \min \Gamma_{t-N}^{mh}(\mathbf{x}_{t-N}) + \sum_{k=t-N}^{t-1} ||\mathbf{w}_k||_Q^2 + \sum_{k=t-N}^{t-1} ||\mathbf{v}_k||_R^2 \]

subject to \( F\mathbf{x}_t \leq d, \) and (23a), (23b)

Arrival Cost Recursions:

\[ \Gamma_{t-N}^{mh}(\mathbf{x}_{t-N}) = \frac{1}{2}||\mathbf{E}\mathbf{x}_{t-N} - \mathbf{A}\mathbf{x}_{t-N-1}||_{P(t-N)}^2 \]

\[ p_k^{(\ast)} = (\mathbf{M}^T F_{t-N}^{(\ast)} - 1) \mathbf{EM} + \mathbf{M}^T \mathbf{C}_{\text{meas}}^{i} R^{-1} \mathbf{C}_{\text{meas}}^{d} \mathbf{M}^{-1} \]

\[ p_{t-N}^{(\ast)} = \mathbf{AM} p_{t-N}^{(\ast)} \mathbf{M}^T + \mathbf{Q} \]

\[ p_{t-N}^{(\ast)} = \mathbf{M} p_{t-N}^{(\ast)} \mathbf{M}^T \]

Final Solution:

\[ u_k^{(\ast)} = \bar{u} + x_k^{(\ast)}(end - 1 : end) \]

\[ y_{\text{out},k}^{(\ast)} = \bar{y}_{\text{out}} + [\mathbf{C}_{\text{out} D_{\text{meas}}} x_k^{(\ast)}], \quad k = 1, \ldots, T \]

for outlet gas thermal conductivity measurement. Inequality constraints \( F\mathbf{x}_t \leq d \) were formed to reflect the knowledge about the outlet mass fractions being a number between \([0, 1]\) and that the inlet gas mass fractions of methane and oxygen are between \([0.038, 0.08]\). The covariance matrix for the process noise \( \mathbf{w}_k \) was set as \( \mathbf{Q} = 10^{-2} \times I_{n+2} \) where \( I_{n+2} \) is the identity matrix of size \( n + 2 \). The covariance matrix associated with measurement noise \( \mathbf{v}_k \) was set as \( 0.5 \times I_n \) for the solid temperature measurements and \( 10^{-4} \) for the thermo-conductivity measurement. Finally, the horizon length for the Moving Horizon state estimator was set at \( N = 3 \).

Algorithm I was implemented using CVX [32] in Matlab [13]. The results using the above information are shown in Figures 8–10 superimposed on the results obtained from transient simulation for comparison. Note that the MHE estimates of inlet mole fractions of both \( \text{O}_2 \) and \( \text{CH}_4 \) and outlet mole fractions of \( \text{H}_2 \), \( \text{CO} \), \( \text{CO}_2 \) and \( \text{Ar} \) showed very close resemblance to the outputs coming from the high fidelity model. On the other hand, estimates of outlet gas \( \text{H}_2\text{O} \) and \( \text{CH}_4 \) were marginally accurate due to the inherent non-linearities in these two variables.

The Descriptor Kalman estimate given in [25] was also found and shown in the plots using the symbol (⋆). The Figures show remarkable results with some exceptions. The mean square error values are shown in Table 3 for both the Kalman filter and Moving Horizon Estimation algorithms. The associated Symmetric Mean Absolute Percentage Error (SMAPE) for each estimated variable was also calculated and shown in Table 3 and is defined as follows [33]:

\[ \text{SMAPE} = \frac{1}{t} \sum_{k=1}^{t} \frac{|X_k^{(\ast)} - X_k^{\text{sim}}|}{X_k^{(\ast)} + X_k^{\text{sim}}}, \quad \text{(28)} \]

where \( t \) is the number of data points, \( X_k^{(\ast)} \in [X_{\text{In}O_2}, X_{\text{In}CH_4}, X_{\text{InH}_2}, X_{\text{InCO}}, X_{\text{InCO}_2}, X_{\text{InAr}}] \) denote the estimated mole fractions, where \( m = \text{KAL} \) or \( m = \text{MHE} \), and \( X_k^{\text{sim}} = [X_{\text{In}O_2}, X_{\text{InCH}_4}, X_{\text{InH}_2}, X_{\text{InCO}}, X_{\text{InCO}_2}, X_{\text{InAr}}] \) denote the corresponding simulated mole fractions.
Table 3 show relatively large SMAPE values for estimating $X_{\text{Out} H_2 O}$, $X_{\text{Out} \text{CH}_4}$ and $X_{\text{Out} \text{CO}_2}$. This can be attributed to the deficiency in the low complexity model in which process non-linearities were not taken into account. Nevertheless, the plots indicate reasonable accuracy even for these variables.

As an indication for the extent of observability, the error covariance for each estimated variable was found from the diagonal elements of $\begin{bmatrix} C_{\text{out}} D_{\text{out}} & P_s^{(+)} \end{bmatrix} \begin{bmatrix} C_{\text{out}} D_{\text{out}} & T \end{bmatrix}$ and the last two diagonal elements of $P_s^{(+)}$ where $P_s^{(+)}$ is the steady state value of $P_s^{(+)}$ given by Algorithm I. The values are also shown in Table 3 that demonstrate good observability implied by the small error covariances.

Table 3 also demonstrates that Moving Horizon Estimation outperformed the Descriptor Kalman Filter in almost all mean square error and SMAPE values. The consistency condition (14) was met exactly in all the solutions obtained. Moreover, the average execution time for each iteration using MHE was 0.0145 seconds on a 2.4 GHz Intel Core i-5 desktop computer with 6 GB of 1067 MHz memory. This implementation can also be made roughly 20 times faster using custom, library free, C code generated using CVXGEN [9] which can be used on stand-alone microprocessors if desired. Hence, the execution times obtained are relevant to the time scales and dynamics of the process.

It is worth mentioning however, that using longer horizon lengths; i.e. $N > 3$, will not result in better estimation accuracy due to the inevitable model mismatch between the high fidelity model and the reduced model. Table 4 shows the m.s.e performance for both Kalman filter and MHE when a density measurement is used instead of a thermal-conductivity measurement at the outlet. This experiment used the same tuning parameters stated before and added the same amount of measurement and process noise as before. The results indicate similar performance as to the previous case indicating that thermal conductivity and density measurements at the outlet are interchangeable and provide almost the same amount of observability.

Another test was conducted when neither thermal-conductivity or density measurement is used at the outlet, and only three solid temperature measurements installed at 0.13 cm, 0.31 cm and 1.88 cm from the inlet. The resulting overall mean square error performance was $3.1 \times 10^{-3}$ for Kalman estimator and $5.1 \times 10^{-3}$ for MHE showing the significance of thermal-conductivity/density measurement at the outlet in improving estimation performance. Finally, when only two temperature measurements are used (at 0.13 cm and 0.31 cm from the inlet), the descriptor Kalman estimator provides uninformative estimates with total mean square error of 53.3 due to lack of observability. On the
other hand, the MHE provided informative estimates with a total mean square error of $1.8 \times 10^{-3}$ demonstrating the significance of inequality constraints in improving performance of the estimator.

8. Conclusion

A moving horizon estimation strategy for general chemical reacting flow problems applied to the catalytic partial oxidation of methane on rhodium using simulation was presented. The strategy is to use transient simulations of a high fidelity chemical reacting flow model to collect desired input/output data for subsequent system identification and model reduction. The study demonstrated the possibility of inferring both inlet and outlet mole fractions using only solid temperature measurements dispersed across the ceramic monolith reactor and one thermal conductivity or density measurement installed at the outlet. Estimator stability was guaranteed by insuring observability. A new Moving Horizon Estimation algorithm for descriptor systems was developed with arrival cost calculations that take into account deterministic information using the techniques presented in [25].

Although this simulation study was conducted for a CPOX reactor that is typical for small scale applications, the implications of this work may extend to larger scale applications. However, since the estimator design was tested via simulation, experimental evidence is still required to confirm the observations in this study.

In the reduced complexity model that was captured, only disturbances in the inlet gas $C/O$ ratio was studied since it was found that this variable has the strongest influence on the outlet gas compositions than other unmeasured disturbances. If desired, the effect of other disturbances; i.e. furnace temperature, gas pressure, gas velocity etc. can be captured by identifying several sub-models using the same approach presented.

The estimation accuracy of the linear estimator developed in this study, in terms of mean square error values was in the order of $O(10^{-5})$ with very good performance for estimating inlet $O_2$ and $CH_4$ and outlet $H_2$, $CO$ and $Ar$ mole fractions. On the other hand, the estimation accuracy achieved for outlet $CO_2$, $H_2O$ and $CH_4$ was less successful due to model mismatch effects. Improvement of estimation accuracy will be a subject for future studies using direct filtering techniques, as studied for example in [34].
Figure 10: Comparison between estimated results: True Values (hard line), MHE (dashed line), Kalman Filter (*)

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Table 3: Mean Square Errors with T.C. measurement

<table>
<thead>
<tr>
<th>Species</th>
<th>Kalman [25]</th>
<th>SMAPE%</th>
<th>MHE</th>
<th>SMAPE%</th>
<th>Error Cov.</th>
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<tr>
<td>$X^n_{\text{H}_2}$</td>
<td>$3.0 \times 10^{-3}$</td>
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<td>$X^n_{\text{CH}_4}$</td>
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Table 4: Mean Square Errors with Density Measurement

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<th>Kalman [25]</th>
<th>SMAPE%</th>
<th>MHE</th>
<th>SMAPE%</th>
<th>Error Cov.</th>
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<td>$2 \times 10^{-4}$</td>
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