

# Dynamic features and control perspectives in novel hydrocarbons and biogas reforming processes

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## Introduction

Reforming of hydrocarbons towards  $H_2$  takes place under oxidants such as air/oxygen, steam,  $CO_2$ , and a combination of them. Along with  $H_2$ , large amounts of  $CO/CO_2$  are produced, which either need to be removed in order to enrich  $H_2$ , or can be valorized for the production of high-added value chemicals (syngas-to-liquid processes) [1]. Another application of  $H_2$  as a “green fuel” is power production in fuel cells, ranging from simple domestic use up-to transportation and stationary employment [2].

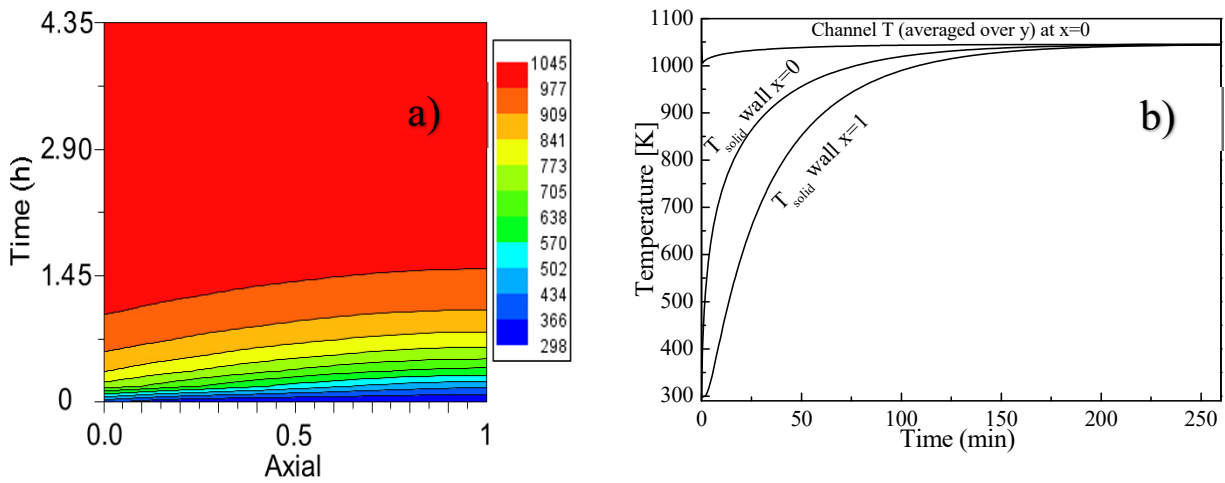
As can be understood, complex dynamic features can be encountered and only through a model-based approach several issues that refer to transient analysis can be tackled effectively. Specifically, during the cold start-up operation, the reactor’s material properties have to be incorporated in a model so that idle times and time scheduling features can be assessed. Furthermore, reformer reactors when integrated to other units such as PSA, shift reactors and  $H_2$  storage units, different time scales emerge that have to be managed [3]. For example, transient simulation might induce peaks, such as hot spots, which cannot be captured by simplified steady-state modeling [4]. Finally and most importantly, control and dynamic optimization techniques are required in order to analyze temperature or composition disturbances [2, 5].

As can be seen, several interesting dynamic features are applied in hydrocarbons and biogas reforming operation. Three of them are briefly discussed in this study: a) the analysis of the dynamic response of a structured catalytic reactor consisting of many (parallel or “distorted”) channels during cold start-up [6], b) its transition to the autothermal reforming mode when biogas is introduced (hot start-up), and c) the control analysis and implementation of PID controllers to an autonomous reforming process coupled with a heat exchanging network.

## Cold and hot start-up of a biogas reforming process taking place in a monolith structure

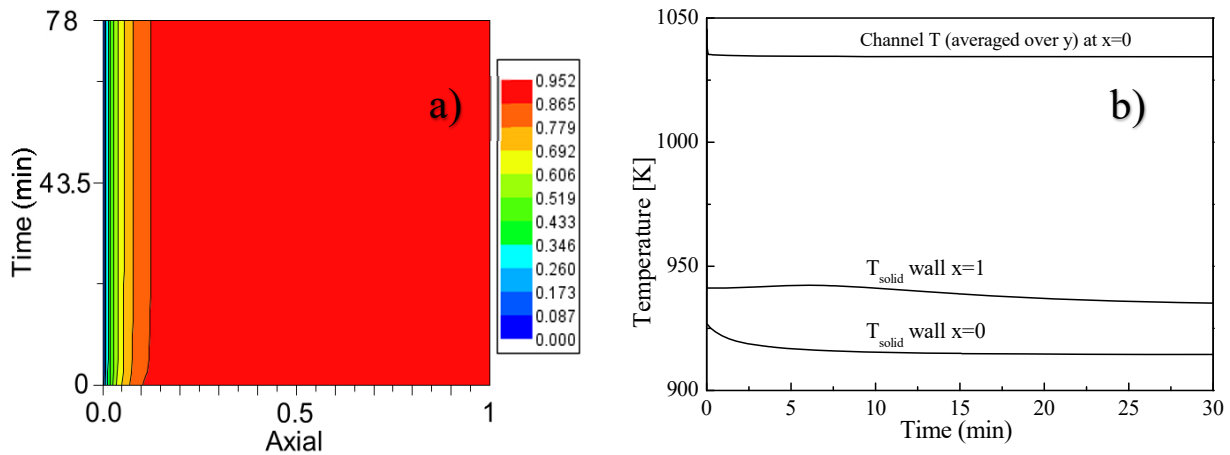
During the cold start-up of a monolith catalytic structure, the solid material has to be heated up to the reforming temperature. In an adiabatic case, no external heating is provided to the reactor, and the heat-up of the reactor’s solid material and catalyst has to be performed exclusively by a preheated inert gas entering at the desired temperature. In this case, the dynamics of the solid reactor are determined by the heat inertia terms of the solid materials (densities and heat capacities), as no other sink/source term (non-reactive case) exists in this mode of operation. Figure 1a depicts the contour plot of the axial monolith’s wall temperature (SiSiC material) as a function of time when air enters the monolith at time  $t=0$  and 1045 K. As can be seen, the solid material’s temperature initiates from ambient conditions (298 K) and needs a significant amount of time to reach the reforming temperature. Specifically, the overall monolith exceeds 977 K after 1.45 h of heating, and reaches the steady-state temperature (1045 K) after 4.35 h. Figure 1b shows that the upper point (dimensionless axial distance:  $x=1$ ) at the monolith’s wall needs more time to reach the steady-state temperature than the point closer to the inlet ( $x=0$ ).

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**Figure 1.** a) Contour plot of the solid outer wall temperature along dimensionless axial distance over time, b) transient temperature profiles of the heating gas in the channel zone and solid temperatures at the outer wall at two different x-points (cold start-up case).

When the monolith has reached the desired reforming temperature ( $t=4.35$  h and 1045 K), the biogas mixture along with  $O_2$  enter the monolith reactor at 1045 K (sustaining a close-to-auto-thermal mode). Due to the fact that solid materials are already at the required temperature, catalytic reactions at the washcoat initiate rather instantly, and methane conversion exceeds 95% (Figure 2a). Furthermore, temperature gradients are not as severe as in the cold start-up operation and show a more reasonable behavior (Figure 2b).



**Figure 2.** a) Contour plot of the  $CH_4$  conversion in the channel along dimensionless axial distance over time b) transient temperature profiles of the reformate gas in the channel zone and solid temperatures at the outer wall at two different x-points (reactive case).

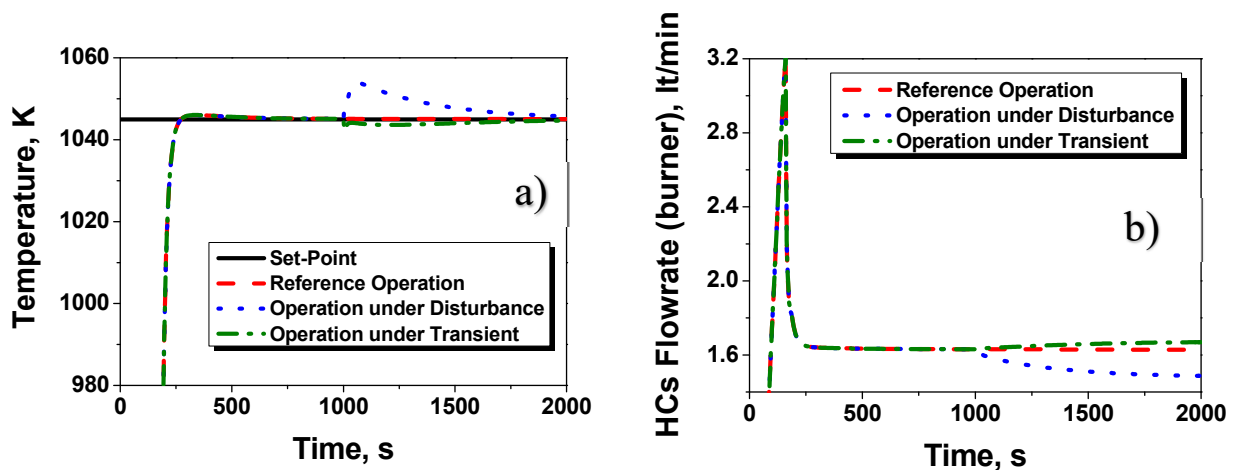
### Control and dynamic analysis of a hydrocarbons or biogas reforming integrated system

As mentioned in the introduction, reforming of hydrocarbons (HCs) or biogas does not take place in one single stage, but is accompanied with purification units and the necessary heat management network. Core objective is to deliver a high purity  $H_2$  stream under minimum utilities. Figure 3 presents a typical reforming integrated system, where several control objectives can arise. The most critical of them are summarized to the controlling of i) unit operation temperature (e.g. reformer, purification), ii) stream temperature (cooling or heating) and iii) product and/or purity flow (e.g. concentration and flow of  $H_2$ ). Satisfaction of control

objectives can be achieved through the manipulation of feedstock (e.g. HCs) and utilities (e.g. air, water, solvents).

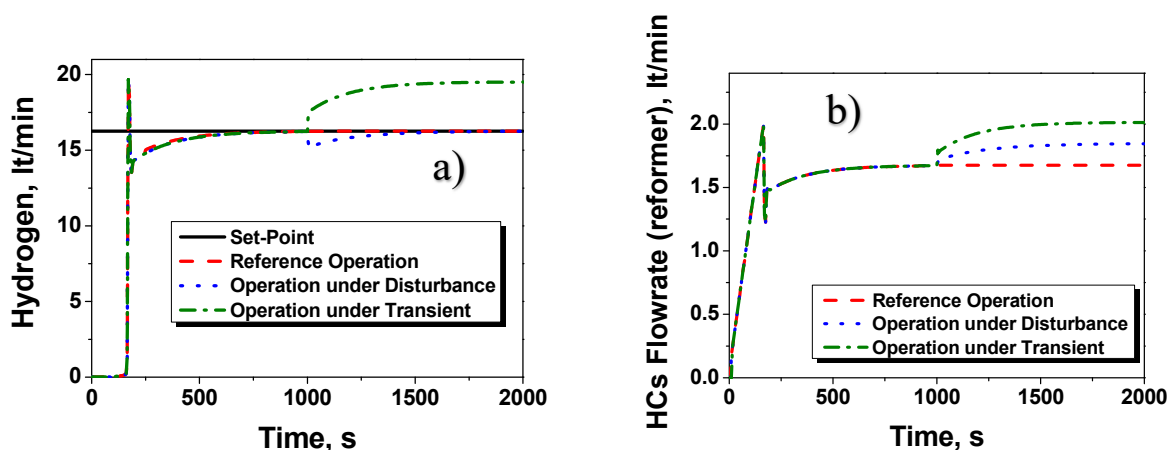
**Figure 3.** An integrated system for the reforming of hydrocarbons/biogas towards  $H_2$  production

Based on the above simplified analysis, the following figures present a control analysis of a typical light hydrocarbons reforming system for the production of  $H_2$ . Three operating modes are studied i) operation in reference state, ii) operation under disturbance (a sudden reforming catalyst deactivation at  $t=1000s$ ) and iii) operation under a new transient (need for  $H_2$  increase at  $t=1000s$ ). In all cases, PID controllers are implemented and optimally tuned via Ziegler-Nichols method. As can be seen in Figure 4a, the reformer operating temperature is controlled adequately in all three cases by the proper manipulation of HCs flowrate at the inlet of the burner. The most critical operation is observed during the onset of the disturbance that creates a temperature overshoot which could damage catalyst structure in the absence of control.



**Figure 4.** a) Temperature control at the reformer and b) manipulation of hydrocarbons at the burner inlet

Similarly, Figure 5a shows how  $H_2$  production is affected at each case. Set point trajectory is reached rather quickly ( $t < 750s$ ) and hence disturbance onset does not seriously affect  $H_2$  production. This however comes also as a result of disturbance rejection prior  $H_2$  exiting the system through previous control actions in upstream processing units. Furthermore, the new transient operating mode is reached even quicker by the proper manipulation of HCs flowrate at the inlet of the reformer (Figure 5b).



**Figure 5.** a)  $H_2$  flow control at the exit of the purification units and b) manipulation of hydrocarbons at the reformer inlet

## Conclusions

As this study demonstrated, hydrocarbons and biogas reforming system have a series of dynamic features that need to be analyzed from a generic modeling perspective. Issues such as cold start-up, introduction of hot feed and control implementation are equally important when integrated systems have to be simulated in various scales of operation. Such an overview aims to predict the dynamic behavior in structured or conventional catalytic reforming reactors for the production of  $H_2$  from different sources (biogas, natural gas, methanol etc) under different modes (autothermal, externally heated etc) of operation, while dynamically optimizing the whole plant when coupled processes are incorporated under system disturbances.

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