***A Bayesian Approach to Reduced Order Modeling in Catalytic Steam Reformation***

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With an ever-increasing demand for power, research and development into clean, renewable energy sources is vital given the uncertain longevity of traditional means. Hydrogen energy has promising potential given its natural abundance and use in fuel cells and other mechanisms. However, these devices require gaseous hydrogen while the majority of this element is contained naturally within water, various hydrocarbons, and other chemical compounds. In order for these devices to be practical, some refining or other hydrogen extraction process is required. Steam reformation is just one of the ways hydrogen can be obtained by reacting steam with methane in a high temperature environment. This creates hydrogen gas at the cost of additional energy input, and the use of a catalyst can limit this to only a certain degree. Maximizing hydrogen production in the reformation process is way to mitigate the impact of the losses.

However, the performance of a catalytic reaction is impacted by a bevy of reactor, environmental, and initial conditions. Time and resources used in process optimization can be shortened through simulation.

It is the goal of this project to develop a reduced order model for catalytic steam reformation. This tool will allow for accurate process-scale predictions across a wide spectrum of possible conditions, both steady state and transient. Not only will this have the capability of performing the aforementioned optimization, but can also prove beneficial for reactor design based on space or performance requirements.

A Bayesian statistical calibration method that has been proven effective by Mebane et al.[1] for modeling $CO_2$ uptake in amine sorbents will be applied. The process uses a detailed reaction network to create two separate models: one that is full scale and another that is of reduced order. This high fidelity model evaluates the network in its entirety, tracking the creation and depletion of each unique chemical species. Then the reaction network is simplified by examining functional relationships to remove all intermediate species; the remaining network serves as the basis for the reduced order model. Using the reaction chain below as an example, a full model would be made from all four reactions tracking the concentrations of 8 species. Then linking reactants to products from each equation as shown in Figure 1 creates a network graph.

$$\begin{aligned} A &= B + C \\ C + D &= E + F \\ B + F &= G \\ E + G &= H \end{aligned}$$

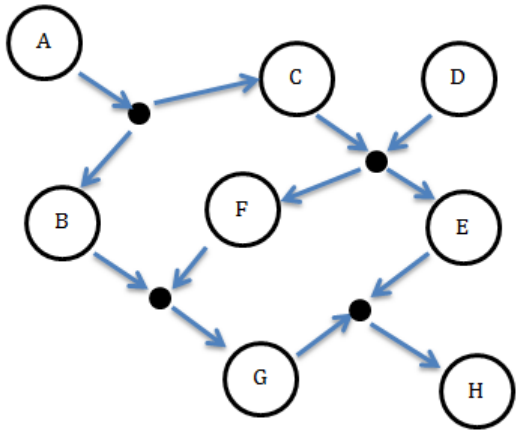



Figure 1: Full Reaction Network Graph Example

Simplifications are made by examining relationships contained in the network. Examining Figure 1 shows that a functional relationship exists between species $A$ and $G$ allowing for species $B$ to be removed. These simplifications continue until the bare minimum of species remain to describe the reaction process, shown in Figure 2.

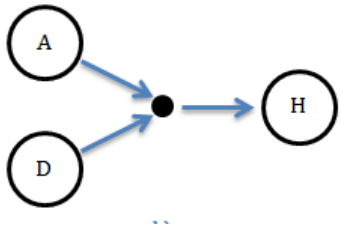



Figure 2: Reduced Reaction Network Graph Example

This new network and corresponding chemical equations are used to develop the reduced model. Removing these intermediate species reduces the dimensionality of the problem, allowing for this model to be less computationally intensive, saving on both time and resources. Model variability that is lost in removing these degrees of freedom is recovered through the use of a Gaussian process-based stochastic function that is defined on an input space consisting of the remaining chemical state variables. The reduced model is thus a stochastic model, meaning that a Bayesian approach to calibration is required. The result of a Bayesian approach to calibration is a stochastic model, all of the realizations of which plausibly reproduce the high-fidelity training data. This approach to reduced order modeling is called dynamic discrepancy, and has been demonstrated in the context of solid sorbent-based carbon capture.[3]

The models and associated reaction network are created based of Xu and Froment's[2] 13-equation reaction chain describing the reformation process. It demonstrates how steam and methane are adsorbed onto open catalyst sites to form various adsorbed radicals which, through several surface reactions, produce hydrogen as well as carbon monoxide and carbon dioxide.

Xu-Froment Steam Reforming Reaction Network:

$$H_2O + L = O^* + H_2 \tag{1}$$
$$CH_4 + L = CH_4^* \tag{2}$$
$$CH_4^* + L = CH_3^* + H^* \tag{3}$$
$$CH_3^* + L = CH_2^* + H^* \tag{4}$$
$$CH_2^* + O^* = CH_2O^* + L \tag{5}$$
$$CH_2O^* + L = CHO^* + H^* \tag{6}$$
$$CHO^* + L = CO^* + H^* \tag{7}$$
$$CO^* + O^* = CO_2^* + L \tag{8}$$
$$CHO^* + O^* = CO_2^* + H^* \tag{9}$$
$$CO^* = CO + L \tag{10}$$
$$CO_2^* = CO_2 + L \tag{11}$$
$$2H^* = H_2^* + L \tag{12}$$
$$H_2^* = H_2 + L \tag{13}$$

This network equates to 16 chemical species coexisting during the steam reformation process needing balanced. A system of ODEs is necessary to track the concentration of each unique species, and because a high number of adsorbed radicals exist in the network, a site limited model is necessary to restrict reaction rates based on the availability of the catalyst surface.

Simulating the environment of a plug flow reactor is achieved through a finite volume method of differential spatial increments governed by the kinetics of a constant stirred tank reactor (CSTR). CSTRs allow for the assumption of a well mixed solution varying only in time. By placing multiple of these in succession such that the exit of one serves as the inlet to the next, a system is created with time and spatial dependence similar to the PFR.

Reducing the Xu/Fromennt network will follow the same process as demonstrated in the example. Optimally, the simplified network will only contain the system's five reactants and products. The reduced model representing the simplified network can then be developed similarly to the prior model. Lastly, Bayes' Theorem combined with the MCMC calibrates the two models finalizing the reduced order model.

**References**

[1] Mebane, David S., et al. “Bayesian calibration of thermodynamic models for the uptake of $CO_2$ in supported amine sorbents using ab initio priors.” Physical Chemistry Chemical Physics 15.12 (2013): 4355-4366.

[2] Xu, Jianguo, and Gilbert F. Froment. “Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics.” AIChE Journal 35.1 (1989): 88-96.

[3] Miller, David C., et al. ”Carbon Capture Simulation Initiative: A Case Study in Multiscale Modeling and New Challenges.” Annual Review of Chemical and Biomolecular Engineering 5.1 (2014).