The goal of this project are to develop dynamic discrepancy reduced modeling (DDRM) approaches for high-order catalytic reactions and to implement these models in the context of device or process-scale simulations. The target reaction chemistry is Fischer-Tropsch.

Over the year ending on August 31, 2018, a model for the catalytic steam reformation of methane based only on reactant and product flows and including discrepancy was derived from data and implemented in the context of a process-scale simulation. The successful completion of this exercise included the development of new computational libraries for DDRM modeling in C++, which is easily connected with other codes essential to the project.

The data used in the model building exercise was the experimental steady-state, temperature-dependent CSTR dataset from Xu and Froment.[1] The gas-phase reactants and products considered in the model were CH_4, H_2O, CO_2, H_2 and CO; thus reducing the kinetic model proposed for their dataset by Xu and Froment from a 15-state system to a 5-state system. Discrepancy functions (Gaussian process stochastic functions of the BSS-ANOVA variety) were introduced in the equilibrium constants and rate constants of the dynamic CSTR model.

The essential strategy of the data-driven model building using dynamic discrepancy is to start with a low number of terms in the expansion of each discrepancy function, and conduct a series of calibrations of the models to data using increasing numbers of terms in the expansion. Each calibration of the model to data is Bayesian and yields a "posterior" distribution of model parameters (which include the coefficients in the expansion of the Gaussian processes), given the calibration data. These posterior distributions can be used to compute a Bayesian information criterion (BIC) model discriminant, the minimum of which specifies the final model. This process is facilitated by the fact that the basis functions used in the expansion of the discrepancy are both orthogonal and ordered.

For the steam reformation model building exercise, each discrepancy function (five in total) depended on the gas phase concentrations (partial pressure) of species appearing in the corressponding reaction, along with the temperature. During the model building process, each discrepancy function was built concurrently, such that each contained the same number of terms. The final form of the discrepancy functions contained six terms each:

$$\delta = \sum_{i=1}^{5} \beta_{i,1}\phi_1(x_i) + \beta_{(1,1),(5,1)}\phi_1(x_1)\phi_1(x_5) \tag{1}$$

where x_i are the inputs to the function, β terms are coefficients and ϕ terms are basis functions. x_i with $i = 1 - 4$ gas-phase concentrations, with $i = 1$ pertaining to the concentration of methane. x_5 is the inverse temperature. All basis functions ϕ appearing in (1) are first-order (and thus linear, although higher-order terms are spectral and nonparametric).

The correspondence of the data-built model with the calibration data from Xu and Froment (in the form of conversion at steady-state) appears in Figure . In the figure, black dots correspond to experimental data points while colored curves represent draws from the posterior distribution. Red curves indicate that the corresponding data points were used in calibration, while blue curves indicate data that was held out of calibration to serve as validation data. Model correspondence to the data was deemed satisfactory.

A model of a large-scale plug-flow reactor was constructed using the calibrated DDRM model for the reaction chemistry. A selection of curves from the posterior distribution, seen in Figure , demonstrates how the stochastic DDRM models behave in extrapolation.
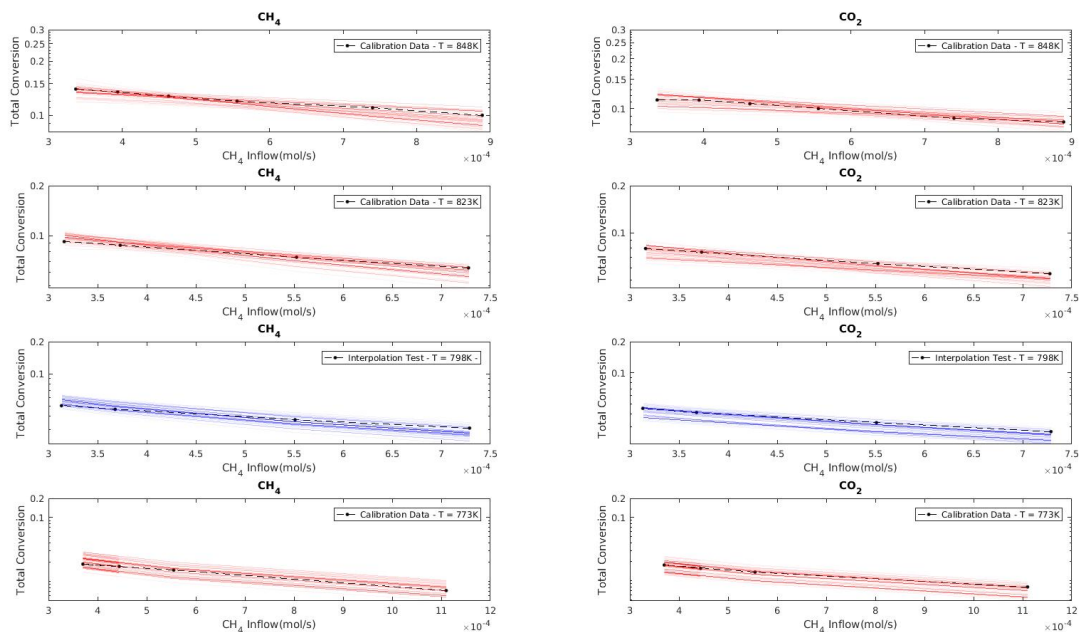
Figure 1: Calibration data from Xu and Froment[1] (black dots) along with DDRM model predictions (colored curves). Red curves pertain to data that was included in calibration while blue curves pertain to data that was held out.

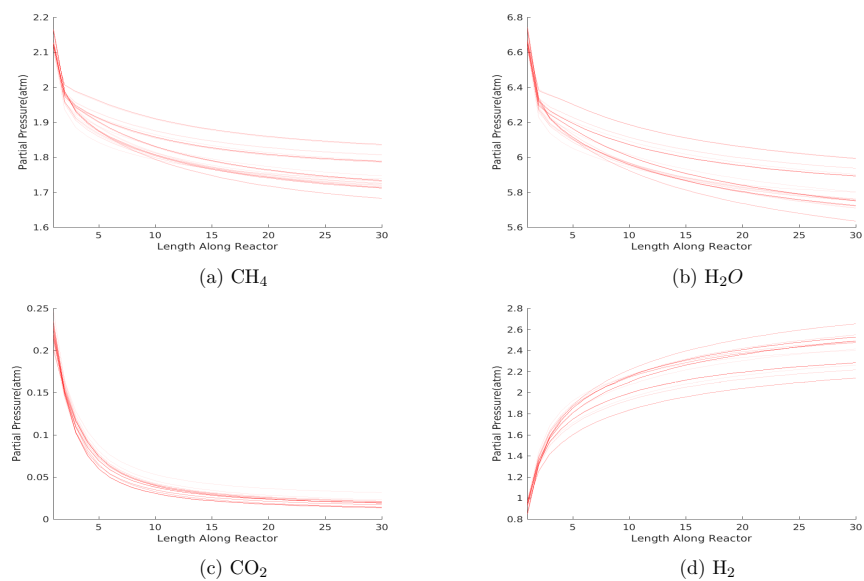(a) CH_4

(b) H_2O

(c) CO_2

(d) H_2

Figure 2: Predictions of the calibrated DDRM model within a large-scale steady-state plug flow reactor model

1. Xu, J. and Froment, G., *AIChE J.* **35** (1989) 88.