ChBE-4746/6746 Group 4 Project

Evaluation of steady-state kinetic models for the $Cu/ZnO/Al_2O_3$ catalytic synthesis of methanol

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Introduction:

Improving accuracy of methanol production models has gained increased interest in research due to the chemicals application in storing energy and to produce important precursors such as ethylene and propylene. Methanol is additionally capable of being produced by renewable carbon sources such as CO_2 and CO which allow a sustainable approach to produce this valuable feedstock. Kinetic models derived for commodity chemicals such as methanol should be able to accurately predict reaction rates under a wide range of reactor conditions and hence, play an important role in the design of industrial processes for large-scale production. Over recent years there has been a debate about which reaction pathway is correct for methanol production under the $Cu/ZnO/Al_2O_3$ catalyst leading to varying kinetic models described in literature based on experts' assumptions of the correct underlying mechanisms.

In this project, we will first attempt to replicate the literature paper's goal of fitting four previously established models as well as the paper's proposed model containing fewer parameters to the given supplementary experimental data set. The paper finally concludes that the model representing the steady state catalytic synthesis of methanol the best is the model that contains the fewest number of parameters while simultaneously being capable of predicting experimental data within one standard deviation, for which the papers new fewer-parameter model is selected as the best one after evaluation of the final metrics described in the literature's results.

The second part of this project aims to implement a machine learning solution that eliminates the need for an expert in kinetics to derive a new model by using the Automated Learning of Algebraic Models (ALAMO) machine learning software to predict a simpler and more accurate model that satisfies the statistical constraint previously discussed (the best model being the one with fewer parameters that can predict a new set of data within 1 standard deviation). ALAMO is a powerful Black-Box modeling software that allows the construction of accurate models from small data sets while ensuring that the models are as simple as possible. ALAMO's methodology is said to be superior to other competing software's such as LASSO. A 2015 academic study showed that ALAMO models are simpler while maintaining higher accuracy than LASSO output surrogate models.[1] ALAMO has been successfully used to model industrial processes such as optimal syngas production as well as producing accurate models for ethylene and propylene plants.[1] Thus, the overarching idea of this project is to determine if ALAMO's capabilities can replicate and output a simpler proposed model, like the novel proposed model outlined in the literature paper, by training the software to the older higher-parameter models along with the supplementary experimental data. ALAMO should theoretically be able to determine which parameters can be eliminated or even changed (e.g., rate dependence power terms) to arrive at a model that predicts the data within one standard deviation and has the least number of parameters.

Part I: Parameter Estimation by Regression (Least Squares Error Minimization):

The goal of the first part of the project is to determine the optimal values of the parameters (the Arrhenius-type coefficients of the lumped kinetic constants) that would best fit the data to different kinetic models. Here, we compare the results obtained for different kinetic models described in the paper and attempt to assess which among them would be the best fit. This is done by determining the minimum value of the mean sum of squares of errors (between the predicted and experimental weight fractions of components) and identifying the kinetic model which would give the lowest such value.

The kinetic models that will be assessed are listed below:

1) Graaf et al.
2) Vanden Bussche and Froment
3) Novel proposed model (6-parameter)

The new model proposed in this paper is supposed to be the best model for the experimental range considered and we will attempt to validate that by solving a series of optimization problems.

Data Set:

The experiments for this project were divided into two: The first set of experiments were done in a CSTR. Then, another set of experiments were conducted under carefully controlled conditions in a set-up consisting of a series of four parallel isothermal fixed bed reactors. Since the reactor is maintained under constant temperature (isothermal conditions), this means that we do not need to account for the energy balance equations which will greatly simplify our objective function formulation. Furthermore, the reactor diameter was kept small enough so that we can neglect any radial variations. As can be seen in the formulation, only axial variations in the gas concentrations will be considered. This assumption simplifies the governing equations and reduces the complexity of the ODE system whose solution is embedded in the optimization formulation.

The data set consists of 234 points, each of which describe the gas mixture composition in weight percentages at the inlet and outlet of the reactor setup. The experiments are conducted over a wide range of reaction conditions to ensure that the rate equations being tested are not biased by narrow sampling ranges. The temperature is varied from 483 K to 533 K, the pressure is varied from 20 to 50 bara and the gas flow rates are varied from 2000 to 10,000 GHSV. Additionally, the amount of catalyst is also varied slightly and is accounted for in the data set by differing values of the apparent catalyst density.

The dataset used in the optimization problem was eventually truncated to include only the 94 samples sourced from the PFR. The other points were sourced from CSTR experiments which would require a different mass balance equation to make use of. We believe this to be an oversight in the original paper.

Pre-processing of the data set prior to starting the optimization problem will not be required as there is not any significant noise expected in the data. Any deviations would be minor and attributed to the variance in measurements while conducting the experiments. A snapshot of the data set is provided below:

E. Experimental data

Table E.10: Experimental values. The density is given as the apparent density. The compositions are in mole percentage.

N	T (°C)	P (bar)	ϕ_V° (mL/min)	T_{in}^0 (°C)	CO_2 *in*	CO *in*	H_2 *in*	N_2 *in*	CO_2 *out*	CO *out*	H_2 *out*	MeOH *out*	H_2O *out*	N_2 *out*	γ	ρ_{app} (kg m^{-3})
141	210	20	66.79	20	22.58	0.005	67.72	9.69	21.70	0.38	65.82	0.96	1.32	9.82	0.98	870
142	220	20	66.79	20	22.59	0.005	67.71	9.69	21.38	0.63	65.30	1.12	1.74	9.84	0.98	870
143	230	20	66.79	20	22.58	0.005	67.79	9.61	20.85	1.10	64.79	1.16	2.25	9.84	0.98	870
144	240	20	66.79	20	22.56	0.005	67.87	9.56	20.07	1.74	63.86	1.36	3.09	9.87	0.97	870
145	250	20	66.79	20	22.55	0.005	67.80	9.64	19.33	2.69	63.51	0.98	3.66	9.83	0.98	870
146	260	20	66.79	20	22.55	0.005	67.80	9.64	18.85	3.32	63.32	0.71	4.01	9.79	0.99	870
147	210	30	65.77	20	22.24	0.005	66.51	11.24	21.16	0.44	64.12	1.20	1.62	11.47	0.98	860
148	220	30	65.77	20	22.21	0.005	66.56	11.22	20.73	0.76	63.60	1.35	2.10	11.46	0.97	860
149	230	30	65.77	20	22.22	0.005	66.57	11.20	20.15	1.30	62.92	1.43	2.72	11.48	0.97	860
150	240	30	65.77	20	22.25	0.005	66.49	11.25	19.36	2.14	62.06	1.37	3.50	11.57	0.97	860
151	250	30	65.77	20	22.26	0.005	66.42	11.31	18.61	2.96	61.37	1.27	4.22	11.58	0.97	860
152	260	30	65.77	20	22.26	0.005	66.41	11.32	18.19	3.50	61.16	1.07	4.56	11.52	0.98	860
153	210	40	65.77	20	22.66	0.005	67.64	9.69	21.37	0.49	64.73	1.50	1.98	9.93	0.97	860
154	220	40	65.77	20	22.79	0.005	67.48	9.72	21.01	0.88	63.85	1.71	2.57	9.98	0.97	860
155	230	40	65.77	20	22.82	0.005	67.47	9.70	20.39	1.45	63.02	1.84	3.28	10.02	0.96	860
156	240	40	65.77	20	22.37	0.005	66.76	10.86	19.40	2.09	62.01	1.53	3.62	11.35	0.97	860
157	250	40	65.77	20	22.26	0.005	66.51	11.23	18.58	2.66	60.74	1.85	4.50	11.68	0.96	860
158	260	40	65.77	20	22.37	0.005	66.37	11.25	18.29	3.09	60.25	1.80	4.88	11.69	0.96	860
159	210	50	65.77	20	22.87	0.005	67.34	9.78	21.29	0.61	63.76	1.83	2.43	10.08	0.96	860
160	220	50	65.77	20	22.97	0.005	67.23	9.79	20.63	1.19	62.51	2.16	3.34	10.17	0.96	860

Figure. 1: Snapshot of experimental data set used in the referenced literature.[2]

Final Optimization Formulation:

The basic framework of the optimization problem will remain the same for all models, however due to differing assumptions and complexity, the models will differ in the number of parameters to be estimated. For instance, the model proposed by Graaf et al. has 12 parameters (Arrhenius coefficients for various rate and adsorption equilibrium constants) whereas the novel model proposed in the paper has only 6 parameters and hence, is a considerably simpler optimization problem. For the formulation discussed here, we will consider only the 6-parameter model for sake of simplicity. However, the same method can be extended to any model in a similar manner.

The problem should be set up so that we find the optimal values of the parameters that, when plugged into the rate equations, should predict values that match the experimental values as closely as possible. The values of the objective functions can be compared between models to get a rough idea as to which model does a better job of predicting the rates.

Variables:

$$K_i = A_i exp\left(\frac{B_i}{RT}\right) = exp\left(\frac{\Delta S^\circ{}_{ads}}{R}\right) exp\left(\frac{-\Delta H^\circ{}_{ads}}{RT}\right)$$

$$k_i = A_i exp\left(\frac{B_i}{RT}\right) = Aexp\left(\frac{-E_A}{RT}\right)$$

Figure 2. Arrhenius equations containing the constants Ai and Bi fitted to the models in the literature.

The above equations in Figure 2 describe the Arrhenius-type dependence of the adsorption equilibrium constants and rate constants on temperature. We need to evaluate the optimal values of the coefficients in these equations.

For the 6-parameter model, some of the adsorption equilibrium and rate constants have been combined to give lumped kinetic constants by making certain simplifying assumptions. This reduces the number of parameters in the optimization problem. For this problem, we have the following parameters:

1) A_{CO_2}
2) B_{CO_2}
3) A_{RWGS}
4) B_{RWGS}
5) k_{H_2}
6) k_{H_2O}

Where the first four parameters are the Arrhenius coefficients of the respective rate constants, and the last two parameters are the temperature independent rate constants.

Constraints:

$k > 0$ and $K > 0$, imposed by logarithmic Arrhenius form
$E_A > 0$ or $b_i > 0$, imposed by bounds
$-\Delta H^\circ{}_{ads} > 0$ or $b_i < 0$, imposed by bounds
$0 < -\Delta S^\circ{}_{ads} < S^\circ{}_{gas}$, checked afterwards

Figure 3. Parameter constraints used for model fitting in the referenced literature.

The above constraints in Figure 3 are general and are utilized to improve numerical accuracy. The last two constraints would not be required for the 6-parameter model since the adsorption equilibrium constants have been combined into simpler lumped fitting parameters based on the derivation.

Objective function:

The governing mass balance function in Figure 4 below is used in the literature for model fitting and is highly non-convex while also being non-linear due to the nature of the rate equations which appear indirectly in the function. This equation gives us a system of coupled ODEs, the solution to which describes the weight fractions of each component in the reaction mixture as a function of axial position down the reactor bed. Solving these ODEs by integrating over the total length of the reactor bed gives us the expected values of the weight fractions at the exit of the reactor. These values can be subtracted from the corresponding experimental values of the gas composition at the reactor outlet to generate the error terms. The mean error for each data point is hence calculated, squared, and summed up for all data points to generate the objective function.

Our goal is to minimize this objective function by adjusting the values of the parameters described previously.

$$\frac{\phi_m}{A_r}\frac{dw_i}{dx} = M_{w_i} \sum_{j=1}^{3} \nu_{i,j}(1 - \epsilon_b)\rho_{cat} r_j$$

Figure 4. Governing mass balance equation used for parameter fitting in the referenced literature.

Where, i = 1, 2, 3, 4, 5 represent the various components involved in the reaction pathway

The above set of equations represent the system of coupled ODEs which need to be integrated over the length of the reactor to obtain the outlet weight fractions If we integrate the above equation with respect to x from $x = 0$ to $x = L$, where L the length of the reactor bed is, we will get the weight fractions at the reactor exit for each of the i components. Let the solution to the above ODE system be given by

$$w_{i,pred} = w_{i,out} \qquad i = 1, 2, 3, 4, 5$$

The sum of mean squared errors can be determined as follows:

$$\boldsymbol{min.\ MSE} = \sum_{k=1}^{94} \frac{1}{5} \sum_{i=1}^{5} (w_{i,pred} - w_{i,expt})^2$$

Figure 5. The mean squared error objective function utilized in the referenced literature through use of outlet weight fractions derived from the governing mass balance equation and experimental data. The outer summation implies that the MSE is being evaluated and summed up for all 234 data points.

Once parameters are fitted to each model. We will perform a 5-fold Cross Validation (CV) analysis as well as the statistical metric “wp” presented in the literature that determines the percentage of correctly predicted data points within one standard deviation. The MSE, CV, and wp values for each of the models were final metrics utilized in the literature to determine which model was the most appropriate for use in industrial process modeling of methanol synthesis.

Optimization Method:

The detailed steps involved in the optimization formulation and the use of ODE solvers will be discussed here. The problem is inherently complex since the coupled ODE system is embedded within the optimization problem.

Initially, we attempted to use Pyomo to solve the problem. However, the need to use **‘pyomo.DAE’** to solve the ODEs within Pyomo proved to be too complex, so we decided to use a standard gradient-free black-box optimizer to solve the problem.

First, we convert all the volumetric flow rates given in the data set to mass flow rates. Then, we set up the system of differential equations after expressing the fugacity terms in terms of respective weight fractions. The basic functions/equations that are required to define the ODE system are mentioned below. These functions are also defined in separate Python code cells prior to starting the optimization formulation.

$$M_{avg.} = \frac{W_{CO2} + W_{H2}}{\frac{W_{CO2}}{M_{CO2}} + \frac{W_{H2}}{M_{H2}}}$$

$$\rho = \frac{P \times 10^5 \times M_{avg.} \times 10^{-3}}{R \times (T + 273.15)}$$

$$\phi_m = \frac{\phi_v^o \times 10^{-6}}{60} \times \rho$$

$$D_r = 6.35 \times 10^{-5}$$

$$A_r = \frac{\pi}{4} \times D_r^2$$

$$1 - \epsilon_b \cong \frac{\rho_{cat}}{1300}$$

$$f_i = \frac{W_i \;/\; M_i}{\sum(W_i \;/\; M_i\,)} \; P$$

The above function converts all fugacity terms which appear in the ODE into weight fractions.

$$k_{CO2} = A_{CO2} \; \exp\left(\frac{-B_{CO2}}{RT}\right)$$

$$k_{RWGS} = A_{RWGS} \; \exp\left(\frac{-B_{RWGS}}{RT}\right)$$

$$k_{H2O/9} = k_{H2} = constant$$

The above equations show the dependence of the lumped kinetic constants on temperature. These are what we will be estimating in the optimization problem.

$$K^o_{P_{CO_2}} = exp\left[\frac{\left\{\begin{array}{c} 7.4114 \times 10^4 + (1.8926 \times 10^2)\,T + (3.2443 \times 10^{-2})\,T^2 + (7.0432 \times 10^{-6})\,T^3 \\ - (5.6053 \times 10^{-9})\,T^4 + (5.6053 \times 10^{-12})\,T^5 - (6.4364 \times 10^1) T\, lnT \end{array}\right\}}{RT}\right]$$

$$K^o_{P_{RWGS}} = exp\left[\frac{\left\{\begin{array}{c} -3.94121 \times 10^4 - (5.41516 \times 10^1)\,T - (5.5642 \times 10^{-2})\,T^2 + (2.5760 \times 10^{-5})\,T^3 \\ - (7.6594 \times 10^{-9})\,T^4 + (1.0161 \times 10^{-12})\,T^5 - (1.8429 \times 10^1) T\, lnT \end{array}\right\}}{RT}\right.$$

These functions indicate the temperature-dependent equilibrium constants which appear in the rate equations.

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{CO}}{dx} = (M_{CO}\,)[(1 - \epsilon_b)\,\rho_{cat}\,(r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{CO2}}{dx} = (M_{CO2})\;[(1 - \epsilon_b)\,\rho_{cat}\,(-1\,r_{CO2} - r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{H2}}{dx} = (M_{H2})\;[(1 - \epsilon_b)\,\rho_{cat}\,(-3\,r_{CO2} - r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{H2O}}{dx} = (M_{H2O})\;[(1 - \epsilon_b)\,\rho_{cat}\,(+\,r_{CO2} + r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{CH3OH}}{dx} = (M_{CH3OH})\;[(1 - \epsilon_b)\,\rho_{cat}\,(\,r_{CO2})]$$

Finally, we have the system of coupled ODEs which we need to solve. Note that the above equations are valid for the 6-parameter model and the VB model. For the Graaf et. al model, we have additional non-zero stoichiometric coefficients and an additional rate equation for the consumption of CO.

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{CO}}{dx} = (M_{CO}\,)[(1 - \epsilon_b)\,\rho_{cat}\,(-\,r_{CO} + r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r} \; \frac{d\,W_{CO2}}{dx} = (M_{CO2})\;[(1 - \epsilon_b)\,\rho_{cat}\,(-\,r_{CO2} - r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r}\ \frac{d\,W_{H2}}{dx} = (M_{H2})\ [(1 - \epsilon_b)\ \rho_{cat}\ (-3\, r_{CO2} - 2\, r_{CO} - r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r}\ \frac{d\,W_{H2O}}{dx} = (M_{H2O})\ [(1 - \epsilon_b)\ \rho_{cat}\ (r_{CO2} + r_{RWGS})]$$

$$\frac{\emptyset_m}{A_r}\ \frac{d\,W_{CH3OH}}{dx} = (M_{CH3OH})\ [(1 - \epsilon_b)\ \rho_{cat}\ (r_{CO2} + r_{CO})]$$

After defining all the required functions and making the necessary unit conversions, we defined the system of ODEs in Python and ran it through the **'odeint'** function in the **'SciPy.integrate'** package. The initial conditions were referenced from the initial weight fractions as given in the dataset. The step-size specified in the solver was restricted due to memory limitations. The end point of the solution array represents the final weight fractions and the MSE was calculated for all data points by looping the ODE solver through all 94 PFR data points and computing the MSE at each point. The total MSE was then obtained by averaging all 94 MSE values.

This piece of code was then input to a black-box optimizer. We chose to use the **'BayesianOptimizer'** function which was one of many gradient-free solvers that we could have used to solve this problem. The parameters to be estimated were defined and the MSE loop was run through the function. The search space was restricted based on literature standards and the number of iterations were limited. We had hoped to continue to run the solver through as many iterations as possible till convergence but could not due to memory allocation issues.

After evaluating the parameters and the minimum MSE value, we evaluated the cross-validation coefficients for each model. This CV(5) metric is calculated by averaging the MSEs for five different 80/20 (training/testing) sets of data. Finally, we plotted the variances in the estimated MSE values for different shuffled training sets in the form of a Gaussian distribution. The results of our code are discussed below:

Results:

The different metrics were evaluated and used to compare the three models taken under consideration.

```
Results: 'TOTAL_MSE'
   Best score: 0.09687748354146937
   Best parameter:
      'Arwgs' : 6.11e+19
      'Brwgs' : -180000.0
      'Aco2'  : 5815000000000000.0
      'Bco2'  : -230000.0
      'kH2'   : 4.6000000000000005
      'kH209' : 292

   Random seed: 2036750233

   Evaluation time   : 118.25650787353516 sec    [99.99 %]
   Optimization time : 0.009905815124511719 sec    [0.01 %]
   Iteration time    : 118.26641368865967 sec    [11.83 sec/iter]
```

```
Results: 'TOTAL_MSE'
   Best score: 0.08889517589755178
   Best parameter:
      'aCO'     : 1110000000000.0
      'bCO'     : -80000
      'aCO2'    : 590
      'bCO2'    : -220000
      'aRWGS'   : 105100000000.0
      'bRWGS'   : -80000
      'ACO'     : 9.102999999999968e-08
      'BCO'     : 2400
      'ACO2'    : 4.4100000000000004e-08
      'BCO2'    : 27000
      'AH2O_H2' : 9.7e-08
      'BH2O_H2' : 140000

   Random seed: 675017982

   Evaluation time   : 185.520277261734 sec    [99.99 %]
   Optimization time : 0.012880563735961914 sec    [0.01 %]
   Iteration time    : 185.53315782546997 sec    [18.55 sec/iter]
```

```
Results: 'TOTAL_MSE'
   Best score: 0.004113656374721943
   Best parameter:
      'aCO2'    : 0.5
      'bCO2'    : 72100
      'aRWGS'   : 3316000000000.0
      'bRWGS'   : -20000
      'AH2'     : 3.9000000000000004
      'BH2'     : 630
      'AH2O'    : 4.006999999999987e-08
      'BH2O'    : 56000
      'KH2O_H2' : 1230

   Random seed: 1257484326

   Evaluation time   : 34.55939292907715 sec    [99.97 %]
   Optimization time : 0.009934425354003906 sec    [0.03 %]
   Iteration time    : 34.56932735443115 sec    [3.46 sec/iter]
```

Fig 6: MSE and parameter estimation in Python for a) 6-parameter model, b) Graaf et. al model and c) VB model

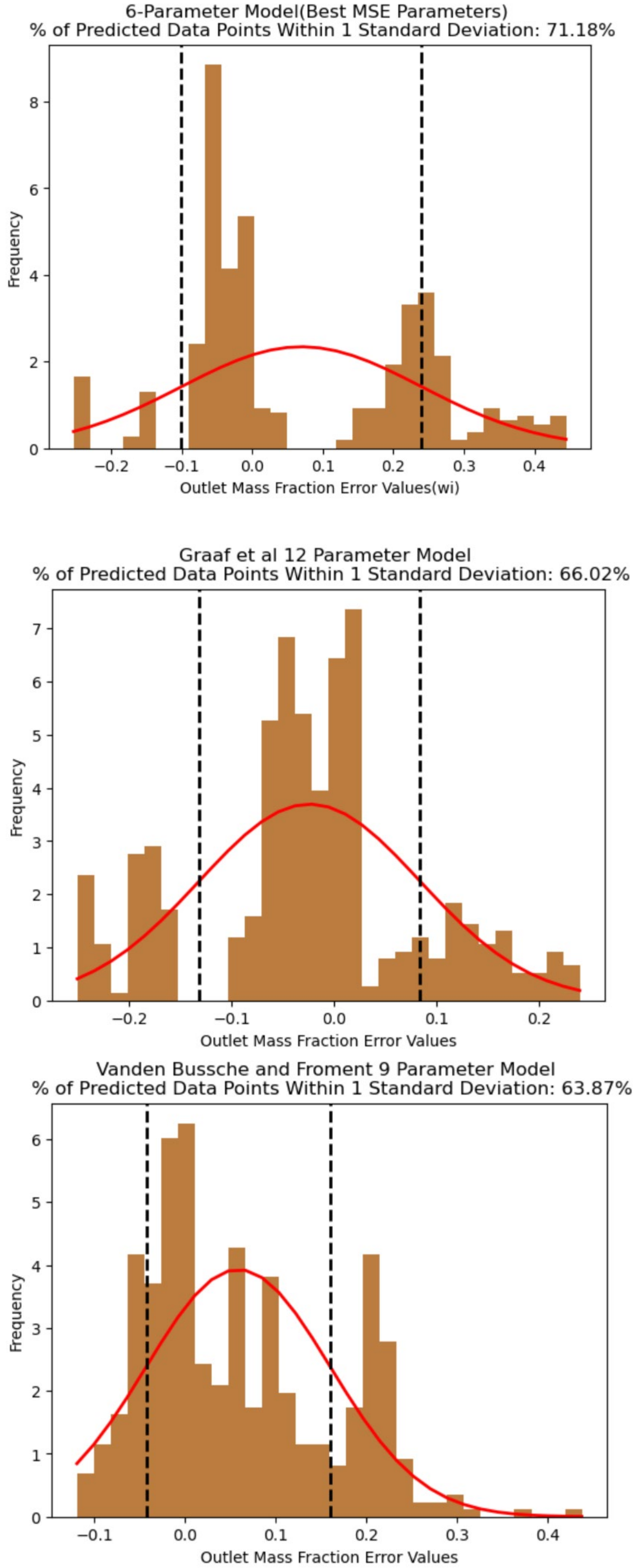


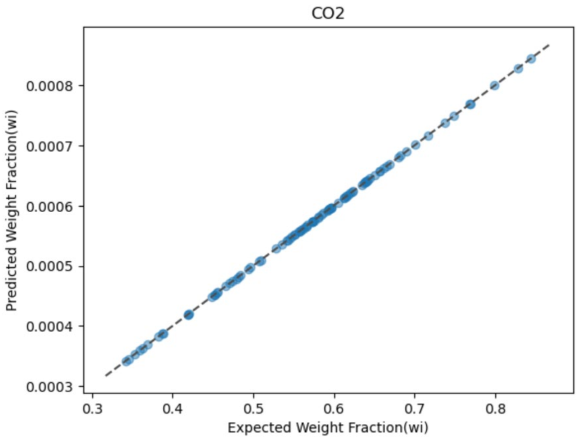
Fig 7: Distribution plots for the MSE deviation/variance from the mean (normalized to zero). Dashed lines represent – σ and σ

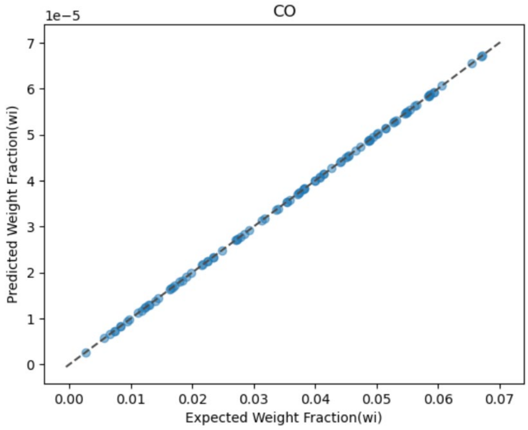
	Total MSE(Full Data Set)	Best MSE(CV5)	CV5	% Correctly Predicted Data Points
6-Parameter	0.0968	0.06673	0.068	71.18
Graaf-12 Parameter	0.0889	0.08224	0.082	66.02
V&B - 9 Parameter	0.0041	0.08222	0.082	63.87

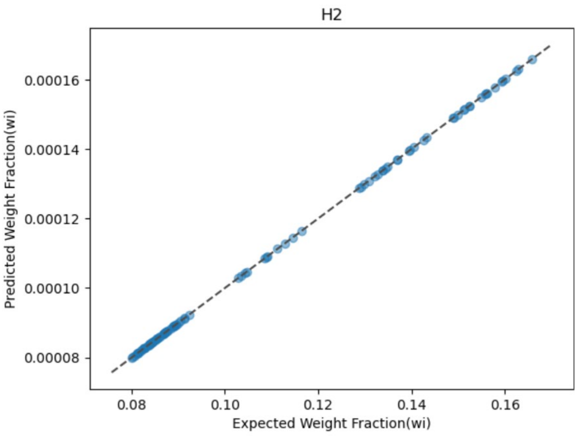
Fig 8: Calculated values of MSE, CV5 and % of correctly predicted points

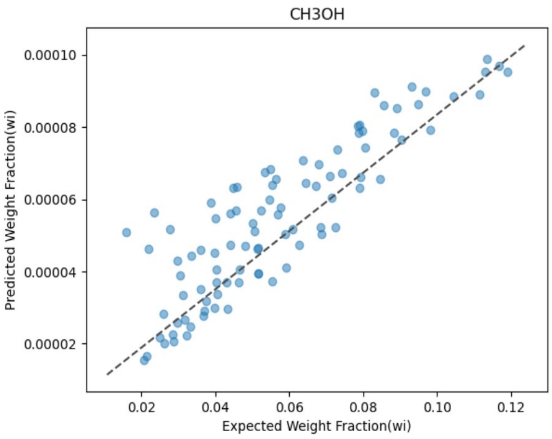
Based on the MSE values only, we would assume that the VB model is the best since it gives the lowest value among all models. However, the 6-parameter model has a lower CV(5) value implying that it is doing a better job at predicting the data when tested with different sets, i.e., it has more consistency and less variance in the results. This is confirmed from the distribution plots which show the 6-parameter model correctly predicting a larger fraction of the data points within one standard deviation ($-\sigma < x < \sigma$) than the other models. Also, it has the lowest number of parameters (simplest) which makes it desirable to use when modelling process equipment such as reactors etc. Our conclusions align with the paper's conclusions that the 6-parameter model does the best job of predicting the rate compared to the other models. Differences in our estimated values from those in the paper can be attributed to the fact that we chose only 94 data points owing to the difference in the method of sampling as explained previously.

Parity plots which show the discrepancy between the predicted and experimental outlet weight fraction values for each component are shown below for the 6-parameter model to give a better idea of the accuracy.









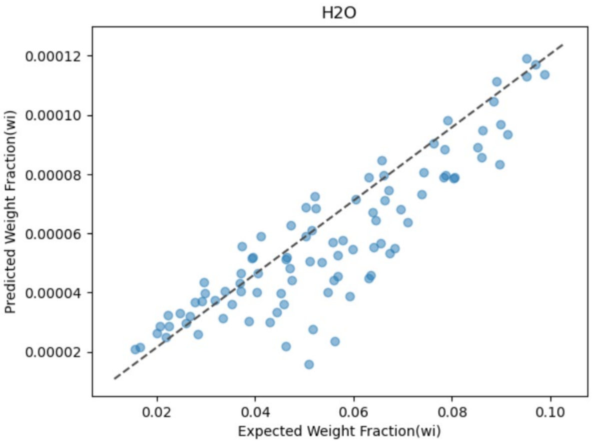


Figure 9. Parity plots for the proposed 6-Paramter model with final paramters taken from the best MSE for all species weight fractions(wi) at the outlet of the reactor.

As can be seen from the parity plots, there is appreciable deviation for methanol and water which was also noted in the literatures work. This can be attributed to the lack of more accurate experiments on methanol and water compositions as stated in the paper.[2]

Part II – Creating a new model using ALAMO:

The goal of the second part of our project is to determine if ALAMO's computational methodology can provide ease of model selection for steady state methanol synthesis under the $Cu/ZnO/Al_2O_3$ catalyst without the need for manual statistical analysis explained in part 1. ALAMO is a regression and classification model learning methodology that constructs the simplest model with the highest accuracy from minimal data sets or Blackbox simulations. ALAMO uses an integer-programming-based best subset technique that compares many explicit transformations of the original input variables. Once a model is formulated within ALAMO, it is tested and enhanced through derivative-free optimization solvers that sample attractive points. ALAMO uses its own sampling method called error maximization sampling (EMS) that allows greater fidelity in constructing a model than traditional DOE methods such as Latin hypercubes and orthogonal arrays. Due to ALAMOs capability of performing its own regression, sampling method, and final statistical model metrics by simply input and output data, we conclude theoretical feasibility of replicating or improving results determined in the literature and part 1 of the project by using a machine learning software. ALAMO additionally has a track record of successfully producing simple and accurate models for reactor and kinetic problems in the field of chemical engineering.[4]

The initial plan was to see if ALAMO could find the most suitable and simple rate determining step models for steady state methanol synthesis under the ZnO/Al_2O_3 catalyst without an expert deriving them through surface and mechanistic insights from literature like the authors of the referenced literature. Once speaking with our PhD mentor Gabriel Gusmao at Georgia Tech who has previous extensive work on the kinetics of methanol synthesis we found out that this method would be very difficult based on the nature of our problem. ALAMO solely takes inputs and output and our governing reactor mass balance equation requires knowledge of the algebraic rate equations to determine the mass fraction concentration profiles throughout the length of the PFR. The experimental data also only includes inlet and outlet mass fractions for which no rate outputs were given for each reactor condition(e.g Temperature, Pressure,etc). If more time was available to our group we would have tried to formulate a type of differential mapping of the concentration profiles across the reactor at each reactor condition. This would allow an extension of information for reactor design by also having a model that would allow improving reactor conditions at different points along the reactor or as a whole by achieving a surrogate model that predicts the weight fractions at each special point along the reactor for a certain condition. We thus decided to validate the results from part 1 and the referenced literature by simply taking each of the 3 models and the fitted parameters from the best MSE to get output rates for each experimental point. We wanted to compare the final surrogate statistical metrics that ALAMO provides a lot with comparing the model equations and size that ALAMO generates for each of the 3 models.

The first step in Figure shows the input and output data entry screen in the ALAMO GUI for the 6-paramter model(same was done for the other 2 models) where the 6 inputs for each data point and 2 outputs(rates at the outlet of the reactor) are entered. The trend of the data before running ALAMO validated an expected trend of rates versus temperature however the histogram of frequency of input data was notable sparce.

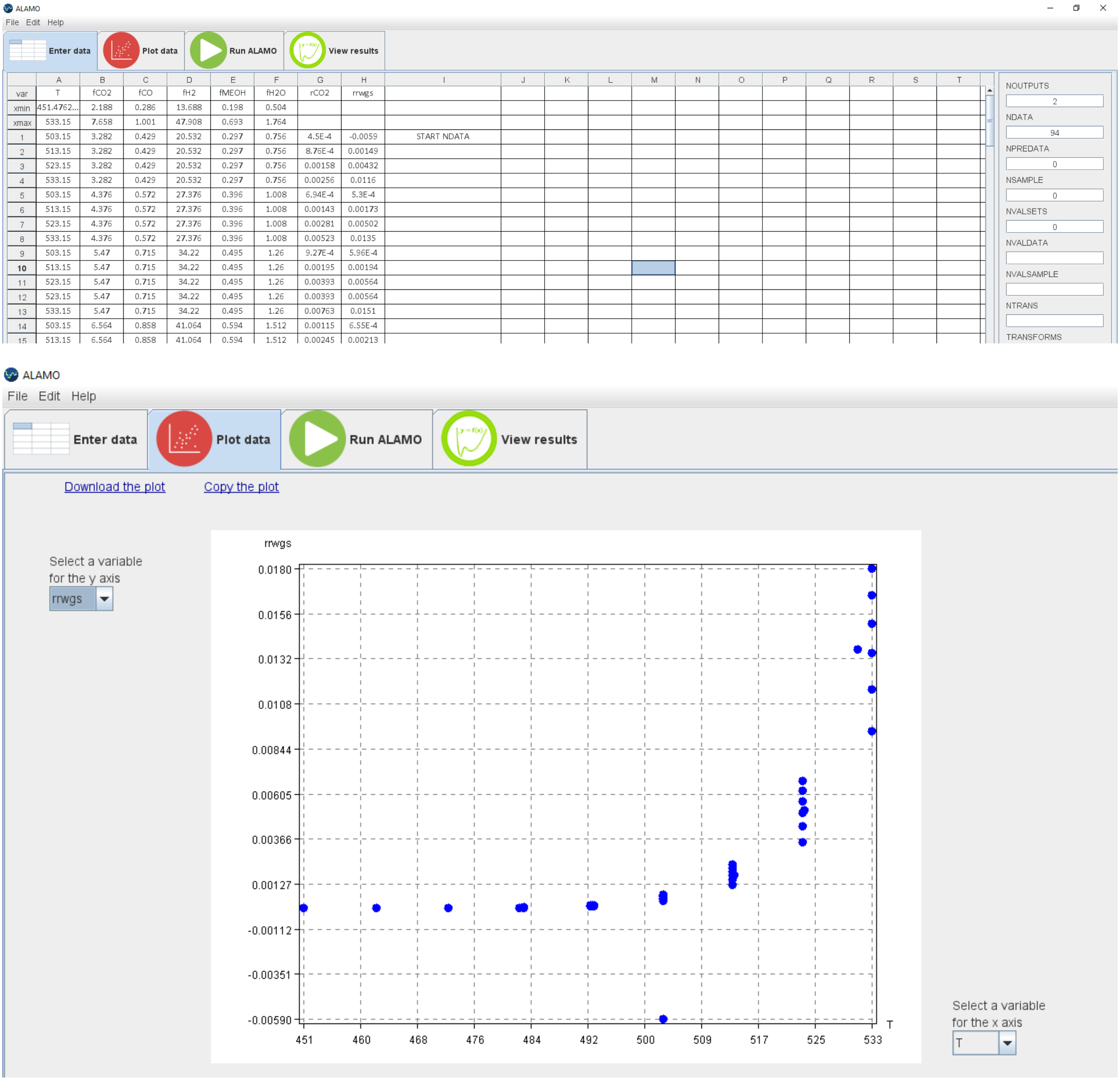


Figure 10. Input user interface for ALAMO showing the 6 inputs variables and 2 output variables for the 6-paramter model(Top) and the generated trend in data for r_{RWGS} vs the input variable temperature.

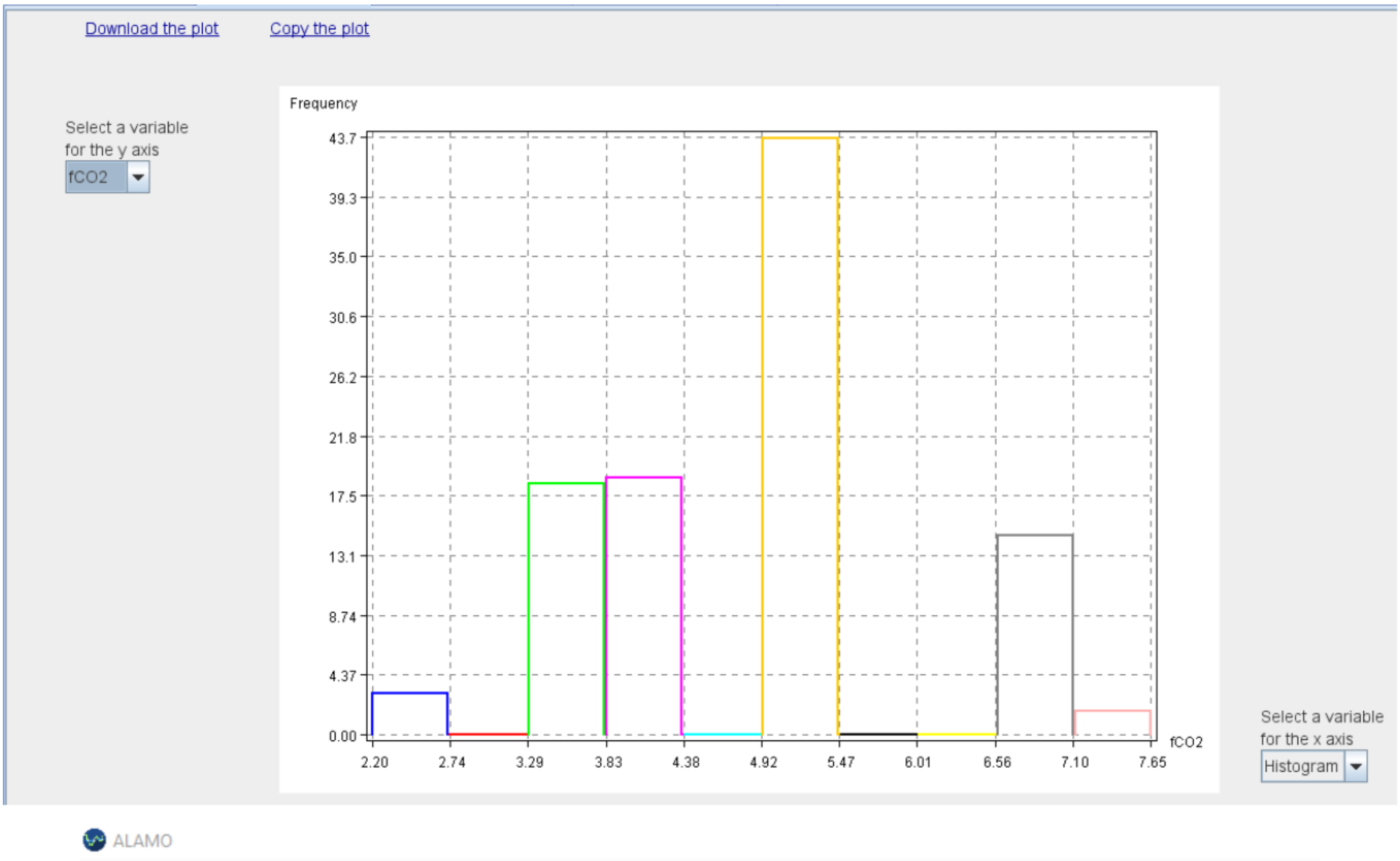


Figure 11. Histogram before running ALAMO for the 6-paramter model depicting the frequency of input variables for the fugacity of CO_2.

The specified basis functions were input to align with the algebraic models to allow ALAMO to more efficiently find a model that closely resembles the rate determining steps. Exponential terms, linear terms, and constant terms were chosen along with the range of powers given in the rate equations as seen below in figure.

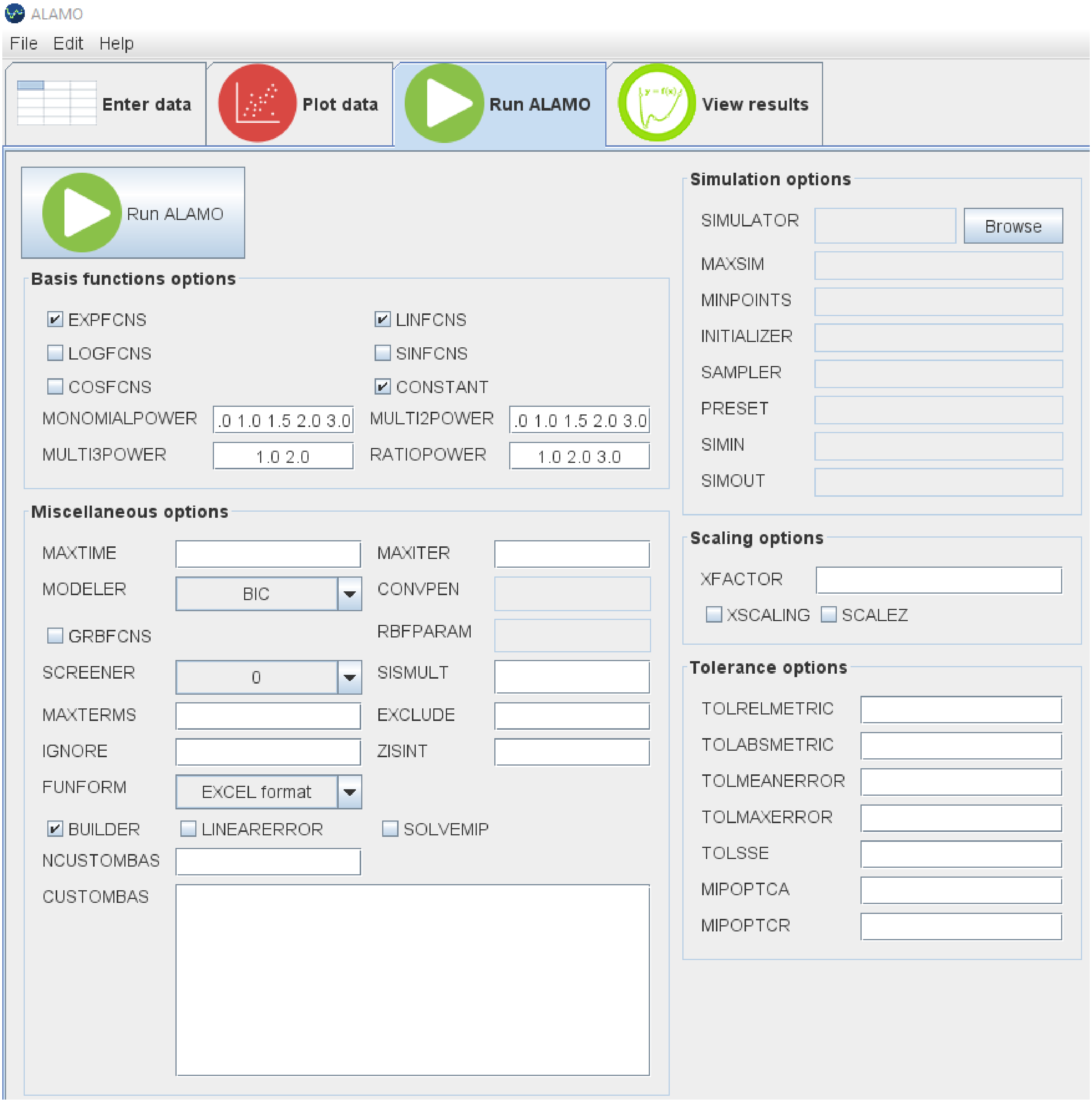


Figure 12. ALAMO GUI screen before running the software depicting the specified basis functions for the 6-paramter model where exponential terms are chosen based on the species rate constants where parameters were fitted in part 1 along with the range of power terms in the derived model.

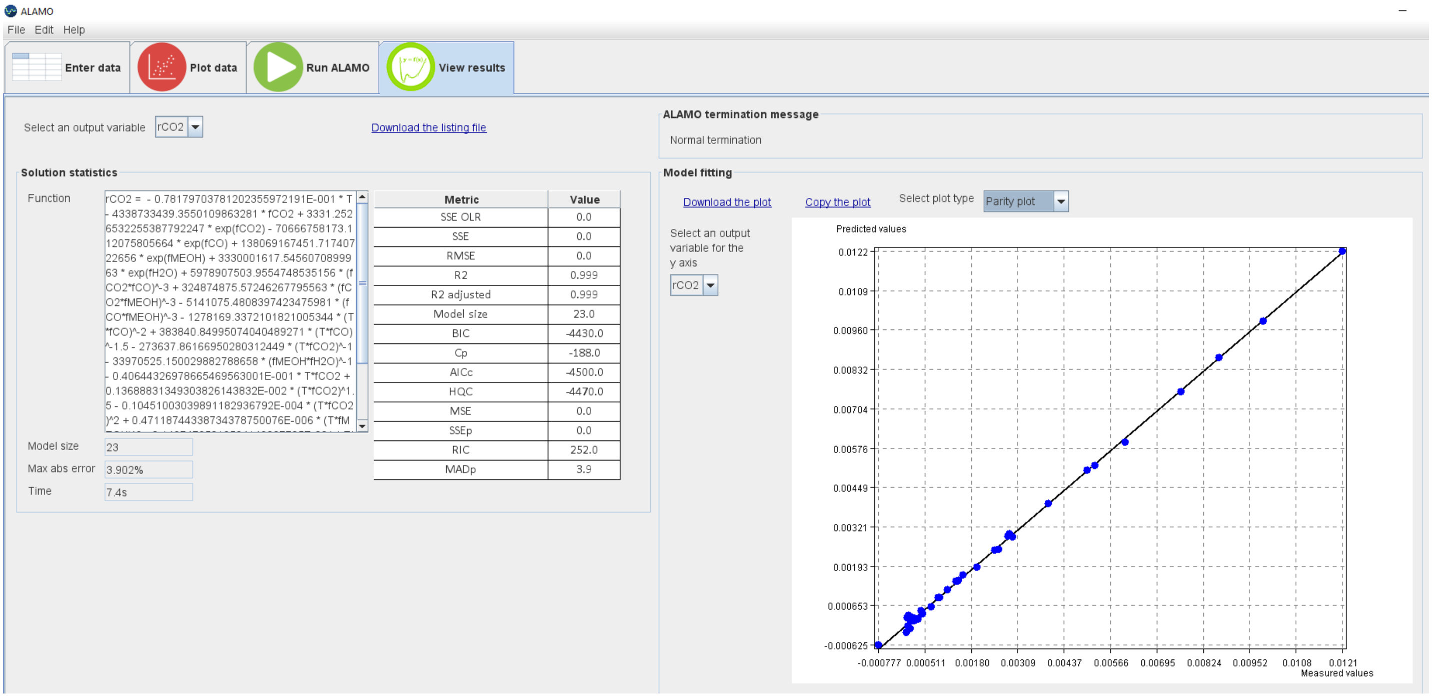


Figure 13. The final output of the surrogate model ,statistical metrics, and parity plot for r_{CO2} for the 6-paramter model in ALAMO.

The figure above shows a relatively good parity plot for the predicted rate of CO2 vs actual rate however for other rate equations such as the reverse water gas shift the parity plot was much moor poor despite the good BIC value. This could potentially be caused by overfitting some noise in the data, outliers in the data for which the BIC is less sensitive to, and model misspecification for smaller rates(most of the poor parity plot values for each of the models reverse water gas shift equation were centered around the smaller rate values).

The final metrics and model size generated by ALAMO for each of the models is depicted below in figure. Dr. Sahinidis(our other mentor) who is the CEO and co-founder of The Optimization Firm for which ALAMO is a product of mentioned that in case of similar BIC ties for our problem, the best model is the one with the lowest model size. According to the final results the lower 6-paramter model has similar range values for the rate of CO2 (the lowest BIC is the most accurate model) across all models while having the smallest model size. The reverse water gas shift reaction model had a much better score for the Vanden and Buscche model however it was hard to determine if the 6-paranter model outperforms due to smaller model size as the difference in BIC between the two are much larger(1000 BIC difference). The Graaf et al. 12 parameter model also had a much better score for the rate of CO but due to the other two models not accounting for CO in their mechanistic insight derivations of the models it was challenging to compare to the other models performance without considering some sort of lumping of the BICs. In either case, the 6-paramter model seems to perform just as well as the higher parameter models with a lower model size which has been the overall conclusion in both the literature and the replication of the literature discussed in part 1 of the report.

Table 1. Final metrics for all 3 models generated in ALAMO for model comparison.

Model	BIC	Model Size
6-Parameter r_{CO2}	-4430	23
6-Paramter r_{RWGS}	-3420	20
Graaf 12 Parameter r_{CO2}	-4580	34
Graaf 12 Parameter r_{RWGS}	-3540	25
Graaf 12 Parameter r_{CO}	-7620	25
VB 9 Parameter r_{CO2}	-4380	26
VB 9 Parameter r_{RWGS}	-5430	35

Statement of Contributions:

Karthik Annigeri: Helped with formulations of the project and managing mentor meetings with professors and PhD students.

Nicholas Daponte: Helped with formulations of the project and managing mentor meetings with professors and PhD students.

Daniel Dinakarapandian: Determined proper formulations for part 1 of the project while also editing the jupyter notebook.

Peyton Holston: Performed research and calculations for the necessary terms and equations for the governing reactor mass balance.

Mohammed Zaker: Cross checked and validated terms and equations stated in the referenced literature to make sure calculations were accurate.

Resources

(1)
ALAMO Modeling Tool | The Optimization Firm. https://minlp.com/alamo-modeling-tool (accessed 2023-02-17).
(2)
Slotboom, Y.; Bos, M. J.; Pieper, J.; Vrieswijk, V.; Likozar, B.; Kersten, S. R. A.; Brilman, D. W. F. Critical Assessment of Steady-State Kinetic Models for the Synthesis of Methanol over an Industrial Cu/ZnO/Al2O3 Catalyst. *Chemical Engineering Journal* **2020**, *389*, 124181. https://doi.org/10.1016/j.cej.2020.124181.
(3)
Slotboom, Y.; Bos, M. J.; Pieper, J.; Vrieswijk, V.; Likozar, B.; Kersten, S. R. A.; Brilman, D. W. F. Supporting Information: Critical Assessment of Steady-State Kinetic Models for the Synthesis of Methanol over an Industrial Cu/ZnO/Al2O3 Catalyst.
(4)
Wilson, Z. T.; Sahinidis, N. V. The ALAMO Approach to Machine Learning. *Computers & Chemical Engineering* **2017**, *106*, 785–795. https://doi.org/10.1016/j.compchemeng.2017.02.010.