Data-driven System Identification for Silver Nanoparticle Production in Modular Reactors

Ganapavarapu Sai Tarun[1], Rohan Saswade[2], Nirav Bhatt[3*], and Sridharakumar Narasimhan[4]

1, 4 Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai-600036, India;

2, 3 Department of Biotechnology, Indian Institute of Technology Madras, Chennai-600036, India

**Corresponding author: niravbhatt@iitm.ac.in*

Highlights

- Demonstrated inadequacy of linear models while modeling continuous flow modular reactors for silver nanoparticle synthesis
- Formulated a Non-linear Auto-Regressive Exogenous Neural Network model that showcased superior performance
- Proposed non-linear model demonstrated a 10-fold validation score of 0.9561

1. Introduction

Nanoparticles have garnered immense importance recently in a myriad of fields. But the key to its widespread use lies in the commercialization of the synthesis [1]. In the last decade, there was a rapid shift from batch to continuous reactors for large-scale synthesis. In particular, micro and milli- reactors were sought-after. They offer many advantages, such as higher surface-to-volume ratios and high heat and mass transfer rates [2]. Furthermore, these reactors allow for a high throughput design by increasing the number of reactors in parallel. Thereby facilitating industrial applications as higher throughputs are essential for commercialization. Despite these benefits, they pose many challenges in terms of mixing. Microreactors involving single-phase reactions will have only diffusion effects, which warrants the addition of an organic capping agent for better mixing. This addi- tion leads to difficulty in end use and size tunability [3]. New reactor configurations such as Corning Advanced Flow Reactors (AFR) provide better mixing because of their heart- shaped design, which induces advection effects in the flow [4].

2. Experimental Procedure and Modeling

A. Experimental Setup and Instrumentation

We assembled the setup for the production of silver nanoparticles (AgNPs) in the Corning AFR. The raw materials employed are Silver Nitrate (AgNO3), Sodium Borohydride (NaBH4), and Tri-Sodium Citrate (TSC). All the mentioned salts are procured from Sigma Aldrich. Additionally, we use deionized water from milli-Q to prepare solutions. Essentially, the reaction to produce AgNPs is between AgNO3 and NaBH4 in the presence of TSC. NaBH4 is a potent reducing agent used to reduce Ag+ ions. TSC is a milder reducing agent that will act as a capping agent in the reaction. The reaction temperature is set to 60°C. The two input streams to the reactor are $NaBH_4$, using a High-Performance Liquid Chromatography (HPLC) pump, and precursor solution of $AgNO_3$ and TSC in equal proportion, using a syringe pump. The output is collected in a beaker placed inside an ice path. This addition is to halt agglomeration of the sythesized nanoparticles. For the analysis of silver nanoparticles produced we have employed spectral analysis, using a Jasco V-630 spectrophotometer, and Transmission Electron Microscopy (TEM). Spectra is measured in the range of 350 to 800nm, with 1nm increments. The protocol involves mixing equal parts of the product obtained with 0.3mg/ml Bovine Serum Albumin (BSA) solution, and letting it cool for 2 hours. Then the solution is drop-casted onto a carbon mesh grid of mesh size 200, and is then left for natural drying.

B. Model Development

We fitted the 6 models typically used in system identification of processes: (i) linear state-space, (2) output-error model, (3) auto-regressive exogenous, (4) auto-regressive moving average exogenous, (5) Box-Jenkins model and Non-linear Auto-Regressive Exogenous Neural Network (NARX-NN) model

3. Results and discussion

Figure 1 shows performance of different models described in the previous section. The trained NARX-NN model performs well. The R^2-value of the validation model is 0.9561. This value indicates that the model between the peak values of absorbance and the flow rates of reactants is a good fit. The residual analysis further demonstrates that there are no patterns and the errors showcase properties of white-noise. The model parameters are tuned to yield steady state when zero input is provided. This is achieved by fixing biases to zero and employing custom loss functions.

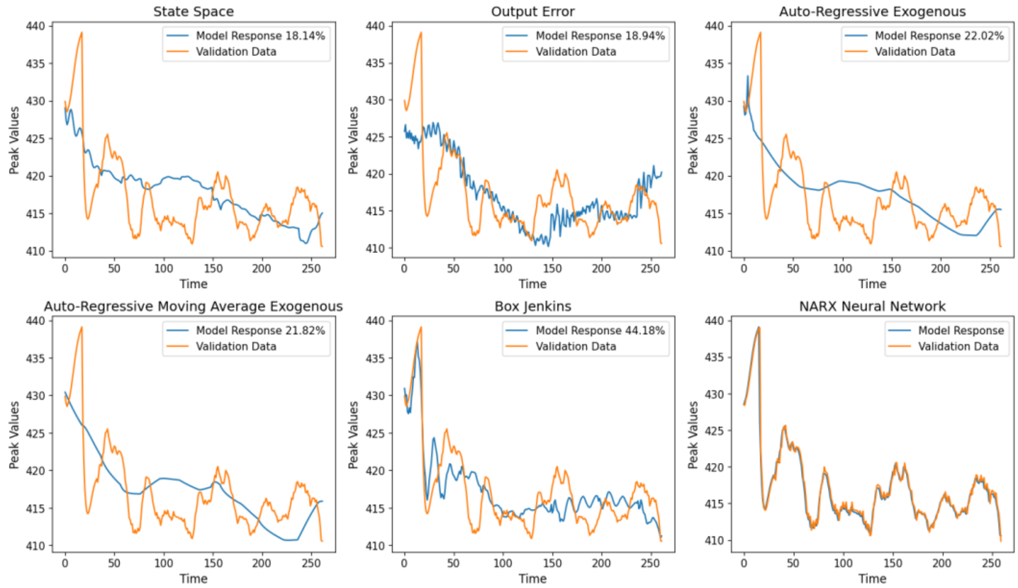

Figure 1. Comparison between model performance of conventional linear models and developed non-linear model. The linear models are evaluated based on their goodness-of-fit with the validation data, while the non-linear model has been benchmarked via 10-fold cross-validation considering R^2-value.

4. Conclusions

In this work, we have modeled the production of silver nanoparticles using various data-driven models. We observe that linear models are inadequate while modeling continuous- flow modular reactors for nanoparticle synthesis, and have demonstrated a poor performance fit with the validation data, with no models achieving a performance fit greater than 50%. We have formulated a Non-linear Auto-Regressive Exogenous Neural Network model (NARX-NN) that has demonstrated a 10-fold validation score of 0.9561. It is shown that the developed NARX-NN model allows for predicting the peak of absorbance spectra at the exit of microreactors using the flow rates of reactants.

References

The reference format is provided below [1 – 3]. [Times New Roman 10].

[1] P. L. Suryawanshi, S. H. Sonawane, B. A. Bhanvase, M. Ashokkumar, M. S. Pimplapure, and P. R. Gogate, "Synthesis of iron oxide nanopar- ticles in a continuous flow spiral microreactor and corning® advanced flowTM reactor," *Green Processing and Synthesis*, vol. 7, no. 1, pp. 1–11, 2018.

[2] Y. Gao, B. Pinho, and L. Torrente-Murciano, "Recent progress on the manufacturing of nanoparticles in multi-phase and single-phase flow reactors," *Current Opinion in Chemical Engineering*, vol. 29, pp. 26– 33, 2020.

[3] R. Manno, V. Sebastian, R. Mallada, and J. Santamaria, "110th an- niversary: Nucleation of ag nanoparticles in helical microfluidic reactor. comparison between microwave and conventional heating," *Industrial & Engineering Chemistry Research*, vol. 58, no. 28, pp. 12702–12711, 2019.

[4] S. Suranani, Y. Maralla, S. M. Gaikwad, and S. H. Sonawane, "Process intensification using corning® advanced-flowTM reactor for continuous flow synthesis of biodiesel from fresh oil and used cooking oil," *Chemical Engineering and Processing-Process Intensification*, vol. 126, pp. 62–73, 2018.

Keywords

System Identification; Silver Nanoparticles; NARX Neural Network.