NSF GRFP Research Proposal

OPTIMIZING THE SYNTHESIS OF METAL ORGANIC FRAMEWORKS USING SEGMENTED FLOW TUBULAR REACTOR TECHNOLOGY

Keywords: metal organic framework, scale up, continuous flow processes

I. BACKGROUND

The segmented flow tubular reactor (SFTR) is an exciting breakthrough in the realm of nano-scale technology. I first encountered this reactor during my research at Sandia National Labs (see personal statement), where it showed much promise in scaling up the synthesis of titania nanowires. Due to the limitations of reactor size, high chemical costs, and uncontrollable side effects of chemical impurities, mass production of nanoparticles remains an ever increasing challenge of engineers today. The expansion of a typical batch process will often lead to low quality synthesis due to the inability to control particle size and morphology under heterogeneous conditions. This same challenge is also paralleled within the metal organic framework (MOF) industry. How can MOFS, having synthesis routes and material properties that depend on nucleation at a reaction surface, be produced at a large scale where quality is often sacrificed for quantity? Fortunately, the SFTR is able to address this issue in much the same way as it did for nanomaterials. The key principle behind the design is the segmentation of the reactants into micro-reactors in a continuous tubular process. Each microvolume is separated by an immiscible fluid or gas as shown in Figure 1. Within this arrangement, borrowing from the concept of 'plugs' in plug flow reactors, reagents are perfectly mixed in the radial direction but not in the axial direction, thus removing the possibility of axial back-mixing, and ensuring that all reactants are endure a similar history (residence time and heat exchange). This process allows the synthesis of homogeneous products with narrow particle size distributions, enhanced control of particle morphology, polymorph selectivity and better stoichiometry control.

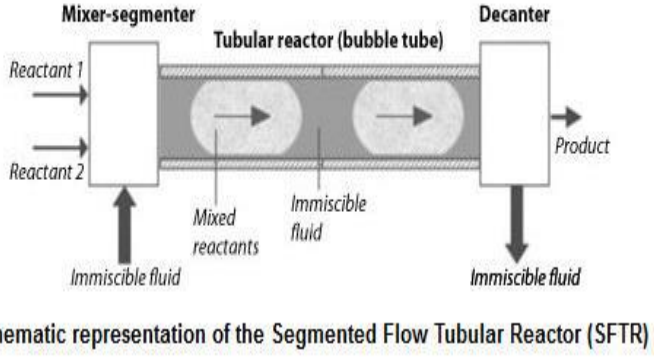

Fig. 1. Schematic Representation of SFTR [1].

II. MOTIVATION

Current literature demonstrates that continuous MOF synthesis is possible, even at the scale of several kilograms per day [2]. The largest MOF manufacturing company, BASF, whose pilot plant is located in Germany, can produce MOFs on order of several kilograms per batch using the solvothermal method. What will be done as the demand for these hydrogen-capturing materials increases, especially as the United States is becoming an increasingly hydrogen-based economy [3]?

III. RESEARCH PLAN

a. *Year I* –Determine Optimal Reacting Conditions for Common MOF Compounds

It is desirable to know exactly what operating conditions the SFTR is expected to perform under before a prototype reactor can be prepared, and thus its effectivity in optimization tested. The respective MOF compounds under analysis include, $Mn_3[(Mn_4Cl)_3(BTT)_8]_2$, $Zn_4O(BDC)_3$, $Cu_3(BTC)_2(H_2O)_3$. These should all be explored due to their ability to their differing levels of hydrogen storage capacity and differing size and geometry. The optimal reacting conditions will also be depend on what pore size is desired for the respective MOFs and what substrate is being used in synthesis.

b. Year II- Determine Optimal Reactor Conditions for the MOF Synthesis

Whereas year I focused exclusively on the chemistry of the MOFs to be prepared and demonstrating that specific reaction conditions generate material with the desired properties, year II will be one of matching those conditions to that of a SFTR. Here, I will be sizing an SFTR that meets all of the requirements given the reaction conditions.

c. *Year III*- Design a Bench Scale Model and Test Performance

At this point in research, it is expected that the prototype reactor can be developed as as bench scale model. Necessary parameters such as tube size, material construction, volume, pumping efficiency and the need for a cooling or heating bath have been determined based on analysis in years I and II. The performance will have to become compared against traditional MOF synthesis routes such as lab scale layer-by-layer deposition, and microwave synthesis.

IV. ANTICIPATED RESULTS

Just as the segmented flow tubular reactor has shown much promise in optimization of calcium carbonate nanomaterial production [1], it is expected that, it will also be successful regarding synthesis of the three chosen MOF compounds. The many similarities between MOF synthesis and nanoparticle synthesis is what will be exploited in this study, to hopefully achieve similar results. Solvothermal synthesis is useful for growing crystals suitable to structure determination, because crystals grow over the course of hours to days. It is expected that by optimizing the SFTRs models to each respective MOF mechanism, a continuous production of uniform and low–defect material can be achieved over this same length of time or even a shorter duration.

V. INTELLECTUAL MERIT & BROADER IMPACTS

The implications of this research project are far reaching, even beyond its potential to mass produce MOFs and thus meet the demand of our growing hydrogen economy. It has the potential to introduce an energy efficient way of producing compounds designed for energy efficient applications to begin with. Double threat! This projects represents the cross between the chemistry and chemical engineering discipline to address the issues in sustainability that plague our nation. The scale-up of MOFs is not an area that has not been widely studied, and thus this research study represents a much needed contribution to the world of sustainable chemistry.

References:

[1] "Precipitation of nanosized and nanostructured powders: process intensification using SFTR", applied to BaTiO3, CaCO3 and ZnO - Chem. Eng. & Techn., 34(3) 344-352 (2011).
[2] "BASF Develops Method for Industrial-Scale MOF Synthesis; Trials Underway in Natural Gas Vehicle Tanks." Green Car Congress. 5 October 2010.
[3] "Global Hydrogen Fuel Cell Electric Vehicle Market Buoyed as OEMs Will Launch 17 Vehicle Models by 2027, IHS Says". IHS Inc. 4 May 2016. Retrieved 13 May 2016.