

The Impact of Non-Isothermal Behavior on Methanol Steam Reforming
in Wall-Coated Microreactors

Introduction:

Over the past few years, issues such as climate change and the cost of oil have resulted in an increasing interest in the development of alternative energies. Among the many options for alternative energy are proton exchange membrane fuel cells, which show particular promise as a small scale portable power source [1]. However, in order for fuel cells to be viable for mobile power generation, the issue of hydrogen storage, which is both expensive and dangerous, must be overcome. One high efficiency option is to use a microreactor to produce hydrogen on site by the reforming of a high energy per volume fuel such as methanol or green alternatives like ethanol or biodiesel [2]. Microreactors are well suited for fuel reforming as they offer high efficiency, integration of processes, and compactness [3]. .

In a microreactor, reactions occur by way of a catalyst coated on the walls of a set of sub-millimeter channels [4,5,6]. While microreactors are generally assumed to operate isothermally (at the same temperature), heat transfer occurring through the catalytic wall gives rise to a thermal gradient (difference in temperature) across the catalyst. The goal of my project will be to determine the impact of a thermal gradient on the methanol steam reforming reaction in a wall coated microreactor. To do so I will produce and experimentally test a mathematical model of the reaction under non-isothermal conditions. Upon completion of my project I will publish my findings in a scientific journal. The conclusions of my research will be beneficially utilized to increase the efficiency of wall-coated microreactors. In the process of completing my project I will gain advanced chemical engineering knowledge as well as skills in the use of modeling and computational programs which I would otherwise not have learned. The knowledge I gain will be invaluable to me when I graduate from UConn and pursue a career in the energy industry. From there I will be able to continue working towards advances in cleaner energy.

Review of Literature:

The methanol steam reforming (MSR) reaction to produce hydrogen is endothermic; as such the reaction must be heated. Heat transfer through the catalytic wall implies that it may not be valid to assume isothermal behavior. It has long been known that temperature gradients can cause considerable deviations in the expected performance of a catalyst [14]. By developing an accurate model of the reaction, I will be able to utilize these deviations to increase the efficiency and selectivity of microreactors.

Even without a non-isothermal model, several groups have shown the viability of microreactors for MSR [5,6,8,9,10]. They were able to independently achieve over 95% conversion of methanol [8] and 97% selectivity towards carbon dioxide (as opposed to poisonous carbon monoxide) [9]. Microreactors are capable of these high conversion and selectivity percentages because of their smaller size which results in an increase in heat transfer rates as well as a greater exposure of catalytic surfaces [11].

Work has also been done in comparing the performance of packed bed to wall coated microreactors. A conventional packed bed reactor is filled with catalyst pellets in the reactor chamber rather than having the catalyst coated along the walls of a channel. Wall coated reactors were shown to be better than [4,5] or equal to [6] the performance of packed bed reactors in terms of yields and isothermality. In either case, wall coated reactors have a lower pressure drop (as they're more open), so less energy is required to supply the feed stream to the reactor. For these reasons, my project is interested solely in the behavior of the wall coated microreactor as opposed to conventional packed bed reactors.

Various methods have been developed to coat the walls of a microreactor [9,10,12,13]. In these cases a $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ [10,12,13] or $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ [9] catalyst was used.

Experiments were primarily based on different slurry mixtures and drying methods. The most successful of these was a water-based slurry which was applied by filling the microreactor and then drying at 300°C [8]. An alumina layer was previously applied to the microreactor ensure better adhesion of the catalyst to the wall. In this case, the microreactor was made of silicon and was composed of several channels. A field emission scanning electron microscope was used to analyze the thickness and symmetry of the coat. For my project, a similar catalyst and coating method will be used. A scanning electron microscope will also be used to analyze the coating. For simplicity and cost reduction, my microreactor will be made of steel rather than silicon and will consist of a single channel.

While the development of a test rig is important, my project is still primarily concerned with the development of a model of the MSR reaction in the presence of a thermal gradient. In their comparison of wall coated and packed bed microreactors for the MSR, Karim et. al. [5] developed a model for both reactors. Their results showed that the microreactor was relatively isothermal. However, their methanol/steam feed into the reactor was preheated to reactor temperature. The feed stream of the model I will produce will be at room temperature as this reflects the operating specifications of the microreactor Professor Wilhite is working on. Furthermore, the math that Karim et. al. used is lacking in detail. They also don't specify what the physics were that their software used in the development of their model. Besser and Ouyang did a similar study on the preferential oxidation of carbon monoxide [4]. They claimed that their model showed "essentially isothermal temperature distribution in the thin film catalyst." However, they included no data in their paper supporting this statement. Still, my project will be procedurally similar to these two experiments in the development of the appropriate equations and the use of software in creating a model.

Methods:

For the past year I have been working in Professor Wilhite's microreactor lab assisting a graduate student in her research. As such, Professor Wilhite has assured me that I will have full access to his lab at the Connecticut Global Fuel Cell Center (on Depot Campus) as well as the use of the facilities there in. I am already familiar with the staff there as well as much of the equipment. I've already built much of the test stand necessary for running experiments. There are four different gas lines available connected to individual mass flow controllers operated via LabVIEW software. There is a heated bubbler in place for introduction of a methanol/steam mixture to the feed gas. I have already produced the microreactor itself and have drilled holes for four heating elements and six thermocouples (electric thermometers). The heaters for both the bubbler and reactor are controlled by their own PID (proportional-integral-derivative) controllers. The thermocouples are wired to a data acquisition bus which reports to the desktop via LabVIEW software. Two other thermocouples are in place to measure the inlet and outlet temperatures as well. The outlet of the reactor feeds to a gas chromatograph (GC) in the lab which interprets the relative concentrations of the product gasses. A mass spectroscopy machine and a scanning electron microscope are also available at the facility. Therefore, the majority of the equipment I will need is easily accessible.

While the setup we have in place is appropriate for determining yields and the activity of the catalyst, the temperature inside the reactor must be known to determine the thermal gradients experimentally. This is difficult to accomplish as it must be done without interfering with the reaction or the heat transfer as it would normally occur. Therefore, a method for determining this particular temperature must be developed. I have already discussed this issue with Professor Wilhite and we have proposed two possible approaches. One would involve introducing a

thermocouple that would be flush with the wall of the reactor before coating with catalyst. The other involves introducing a fiber optic cable into the reactor chamber and reading the temperature through the cable with an infrared camera.

It should be noted that there is plenty of time for development of a method of reading the temperature inside the reactor as I must first develop my model before any testing can be done. Based on a single cylindrical reactor channel and assuming symmetry, my model will most likely be two dimensional (having radial and axial directions). In developing my model I will need to consider a variety of different factors. These include the rate of reaction (kinetics), flow velocity profile, diffusivity into the catalyst, heat transfer, and mass transfer. First, I will attempt to analytically determine a solution for the temperature gradient. A fair amount of my time on this project will be devoted to researching the literature to determine the appropriate equations describing these variables. In many cases, I will develop the necessary equations from the ground up using basic principles and laws of chemical engineering. Examples include Fourier's Law of heat transfer and the Navier-Stokes equations for momentum transfer in Newtonian fluids.

The difficulty is that all of the variables I will have to consider are interdependent on one another. The solution of the system of equations I develop will therefore require the use of computational software such as MatLab or Mathematica, both of which are provided through the School of Engineering computing services. Most likely, I will be able to only partially determine a solution while the rest of the model will have to be developed using COMSOL finite element analysis software. COMSOL software as well as financial support for purchasing equipment and supplies will be provided through Dr. Wilhite's research group.

Plan of Study:

Next semester I will be taking transfer operations II, process kinetics, and physical chemistry II as well as a chemical engineering special topics course on energy that is being taught by Professor Wilhite. The first three classes are required by my major and are important for me to be able to complete my proposed university scholar project. The course being taught by Professor Wilhite will help expand my general knowledge of the energy industry and also satisfies a requirement for my major.

The first semester of my senior year I will take chemical engineering lab, process dynamics and control, a special topics course on fuel cells, and computational mechanics. In the special topics course I will learn more about fuel cells, thereby expanding my understanding what follows fuel processing. Computational mechanics will cover numerical analysis methods, ordinary and partial differential equations, and finite element techniques as applied to heat transfer and fluid flow. This will help me in my project when working with differential equations and will give me a better understanding of the basis of finite element analysis software.

During the second semester of my senior year I will take the second part of chemical engineering lab, process design and economics, differential equations for applications, and a mechanical engineering analysis course. The differential equations course will further enhance my ability to solve ordinary and partial differential equations as well give me exposure to nonlinear differential equations and their applications. The mechanical engineering analysis course will give me more exposure to applied mathematical techniques in heat transfer and fluid mechanics. Following this plan of study will more than satisfy the requirements of my major. Focusing on advanced differential equations, finite element techniques, and there applications will give me the tools I need to successfully complete my project.

Plan of Study Comparison Form:

Spring 2009

Standard Plan of Study	Proposed University Scholar Plan of Study
CHEG 3124 Transfer Operations II	CHEG 3124 Transfer Operations II
CHEG 3151 Process Kinetics	CHEG 3151 Process Kinetics
Chemistry Requirement (Analytical or Physical)	CHEM 3564 Physical Chemistry II
Engineering Requirement	CHEG 4995 Special Topics – Energy

Fall 2009

Standard Plan of Study	Proposed University Scholar Plan of Study
CHEG 4137W Chemical Engineering Lab	CHEG 4137W Chemical Engineering Lab
CHEG 4147 Process Dynamics and Control	CHEG 4147 Process Dynamics and Control
Engineering Requirement	CHEG 4995 Special Topics – Fuel Cells
	ME 3255 Computational Mechanics

Spring 2010

Standard Plan of Study	Proposed University Scholar Plan of Study
CHEG 4139W Chemical Engineering Lab	CHEG 4139W Chemical Engineering Lab
CHEG 4143 Process Design and Economics	CHEG 4143 Process Design and Economics
	MATH 3410 Differential Equations for Applications
	ME 3257 Mechanical Engineering Analysis

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