Honors Capstone Report

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INTRODUCTION

Fertilizer is mass-produced and used worldwide in agriculture. With a population that is still growing and just reached 8 billion people [1], the need for fertilizer will only continue to grow. Ammonia is a main component of many nitrogen-based fertilizers and is currently one of the largest volume chemicals produced globally [2]. Ammonia is highly energy-intensive to produce on an industrial scale due to the high temperatures and pressures required during its manufacturing process, the Haber-Bosch process (400-550 C, 250-350 bar) [2]. This thermally driven process typically requires significant fossil fuel use, and accounts for 5.5 EJ of global energy use per year [2]. The greenhouse gas emissions from ammonia production alone contribute to 1.2% of annual global emissions [3].

Alternatives to the traditional thermally driven Haber-Bosch process used to generate ammonia have been studied extensively, and using a light-driven photothermal process powered by renewable resources is a promising strategy. The addition of light in this traditionally thermal process will reduce the temperatures and pressures required to produce the ammonia, as shown in **Figure 1** below.
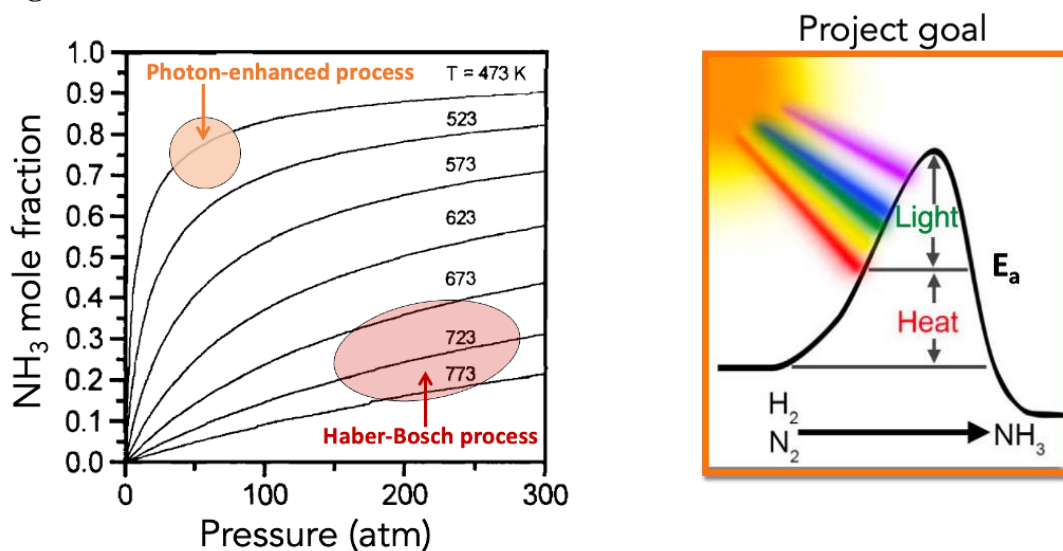

Figure 1. The current temperatures and pressures required to use during the Haber-Bosch process, along with the projected temperatures and pressures required to produce ammonia with the introduction of photons (left). Illustration of how this project will use light to reduce the amount of energy needed to produce ammonia (right).

However, the use of this process for ammonia production must be investigated and better understood to make it more feasible for use in industry.

Ammonia Synthesis Process
The final chemical reaction used to produce ammonia is the Haber-Bosch process, but prior to using this process, additional chemical reactions are required upstream of this reaction to produce a pure form of the reactants needed to make ammonia. The steps required to produce ammonia are shown in **Figure 2** (p. 3).
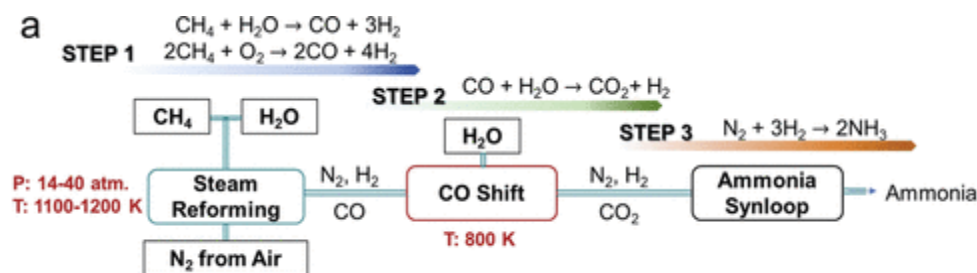
Figure 2: *Lim et al.* The steps required to produce ammonia-based fertilizer. The Sabatier Reaction, another focus of this study, is used to generate methane (CH_4) before Step 1.

These chemical reactions that occur upstream of the ammonia synthesis and fertilizer production process must also be powered by renewable energy processes and have their reaction temperatures and pressures reduced to make the total fertilizer production process less energy intensive.

Previous Work

To present, the Dasgupta Research Group, in collaboration with the Schwank Research Group, has studied the effects of different reaction conditions for the Sabatier Reaction, which is the reaction required to make methane, or CH_4 (used in Step 1 of **Figure 2** above). The groups started with this reaction due to its simplicity and CO_2 reduction capabilities. The Sabatier Reaction is shown below:

$$CO_2 + 4H_2 \xrightarrow[pressure+catalyst]{400°C} CH_4 + 2H_2O \tag{1}$$
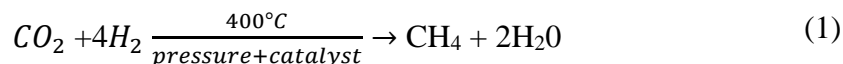
The groups have successfully used TiO_2 with Ru particles in the presence of a UV light to reduce the temperature and pressure required to generate methane. The results of these experiments are shown in **Figure 3** below.
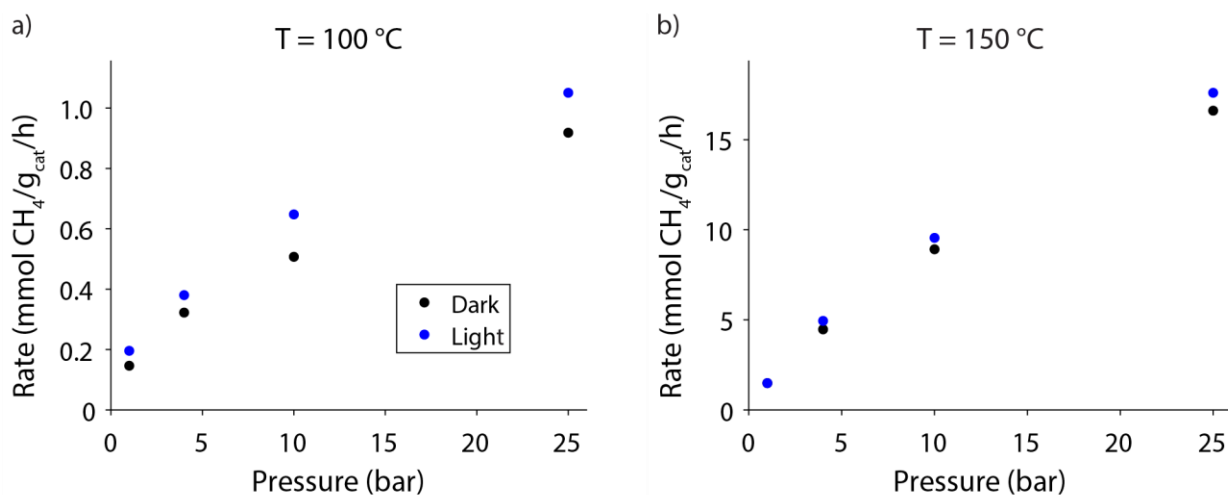

Figure 3: Methane formation rates using the batch reactor under varying temperature, pressure, and light conditions.

All reactions to date have been performed in a batch reactor system[1]. Batch reactor systems involve introducing reactants at the start of the reaction, followed by monitoring the gas composition with respect to time. A picture of the batch reactor system and batch reactor currently used are shown in **Figure 4** below.
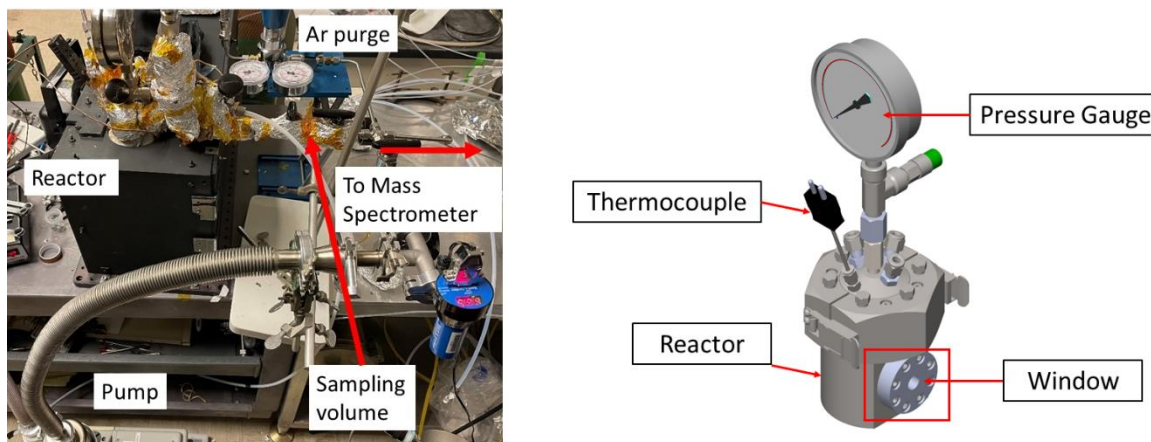

Figure 4: Picture of current batch reactor system (left) and batch reactor (right) currently used. The small reactor window compared to the large gas chamber creates a lot of dead volume in the reactor.

The mass spectrometer in the system is used to measure the composition of the reaction products, while the pump and Ar purge are used to clean the system lines after use. A UV light is shined into the reactor window to add energy to the reaction. The reactor and UV light are covered for safety and efficiency when shining the light into the reactor. The sampling volume is the volume of gas that is sent to the mass spectrometer for measurements.

The current batch reactor system design has several limitations: 1) there is a large amount of dead volume of gas, which makes the reaction inefficient, 2) there is a large amount of downtime between the stages of the reaction, and 3) the batch reactor system is a completely manual process.

On the other hand, flow reactor systems allow for the continuous introduction of reactants, generally allowing for more rapid data collection and analysis. Additionally, using a flow reactor system in lieu of a batch reactor system can decrease the downtime between stages of a reaction. In the synthesis of chemicals such as ammonia, flow reactor systems are more industrially relevant than batch reactors. Testing using the lab-scale flow reactor is an important step prior to the eventual design and implementation of a pilot-scale reactor. Designing the new flow reactor system was my task for my capstone.

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[1] *Batch Reactor System/Flow Reactor System* refers to the entire system used in the chemical reactions, while the *Batch Reactor / Flow Reactor* refers to the chamber where the gases react with the catalyst.

OUTLINE OF PROBLEMS ADDRESSED

1. Convert the batch reactor system to a flow reactor system to allow for more rapid data collection and make this greener solution more suitable for industrial use.
2. Test different temperature and pressure combinations to improve product yield for the Sabatier and Haber-Bosch alternatives.

METHODS

The requirements for the flow reactor and flow reactor system were identified prior to beginning the design of the reactor and system. The relatively high temperatures and pressures used in the light-driven photothermal process were considered when designing each system component.

Flow Reactor System Requirements

The following requirements were developed prior to the design of the flow reactor system:

1. Gas pressure up to 30 bar
2. Ability to preheat the gases to at least 100°C
3. Low gas flow rates, <50 standard cubic centimeters per minute
4. Ability to control flow rates in 1% increments
5. Modular, automated design

The flow reactor system pressure will be constant throughout the gas lines after the gases are mixed, so each component of the system must be able to withstand a gas pressure up to 30 bar. Preheating the gases prior to their interaction with the light and catalyst will allow improve the efficiency of the reaction, as less energy will be wasted in the heat transferred from the hot catalyst to the colder gases.

Low flow rates are ideal for the flow reactor system to improve the product formation rate, as the gases will have more time to react with the light and catalyst. Fine tunability of the flow rate will enable the different flow rates to be tested with more accuracy. System modularity was desired so that different system components could be switched when required by the different reaction conditions tested. For example, the gases fed into one of the lines will be swapped when swapping testing from the Sabatier Reaction to the Haber-Bosch process. Finally, automating the system will reduce the risk of user error and allow for more continuous testing.

Flow Reactor Requirements

The flow reactor had additional requirements to those required for the overall system. These requirements are shown below:

1. Gas pressure up to 30 bar
2. Temperatures up to 200-250°C
3. Measure the temperature in one of these two locations: wall of the reactor and the catalyst
4. Independently control catalyst and gas temperatures
5. Light transmission range of 300 μm – 800 μm

6. Minimize gas dead volume
7. Easily load and unload the catalyst

The gas pressure required in the flow reactor is the same pressure required throughout the flow reactor system, but the maximum temperature is higher within the reactor due to the higher temperature required for the catalyst. Independently controlling the catalyst and gas temperatures is required because the temperature of the catalyst in the reaction is the temperature that controls the reaction, and this temperature will have to exceed that of the gases.

Minimizing the dead volume of gases within the reactor will improve the efficiency of the system and improve the accuracy of the experimental results. Currently, it is hard to determine what the actual yield rate would be under illumination since most of the reaction is happening in darkness. Finally, the flow reactor system will test different catalysts – to make the testing process efficient and accurate, an easy method to load and unload the catalyst from the reactor is required.

RESULTS

Flow Reactor System Design

Using the requirements defined above, the flow reactor system design is shown in **Figure 5** below.
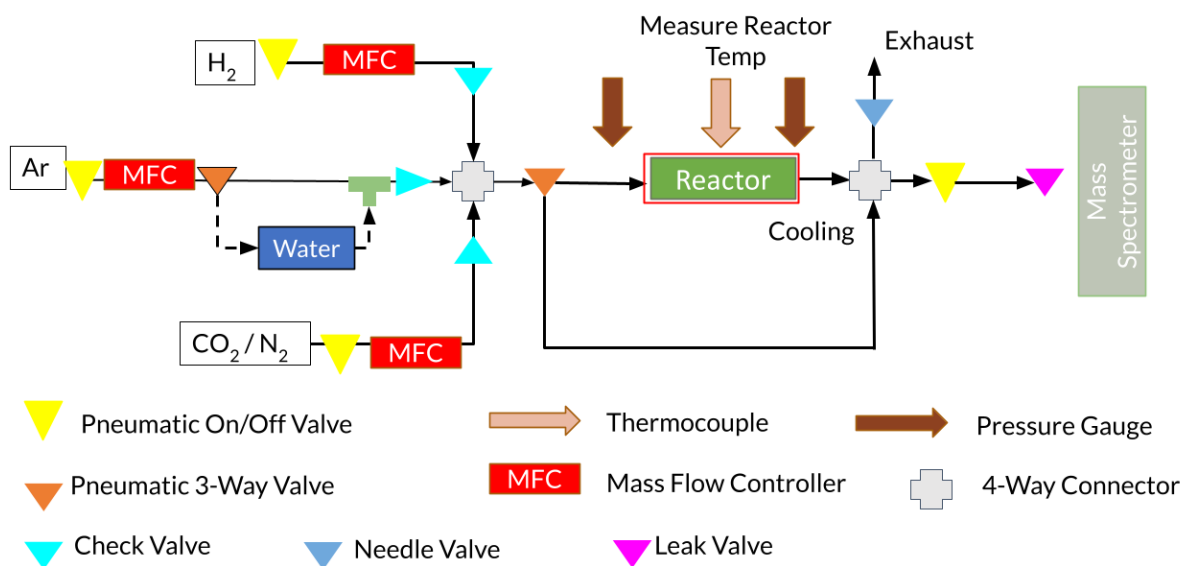

Figure 5: Flow reactor system design. The new system design will allow for faster measuring and reduce the amount of manual work required to run the system.

The different system components shown above help satisfy the design requirements defined above, as well as contribute to the safety and efficiency of the system.

Pneumatic valves will be used in the system to automatically control the flow paths of the gases. Check valves are placed in the system to prevent the gases from backflowing. The needle valve used downstream of the system will be used to maintain the system pressure throughout. The three-way valve shown directly upstream of the reactor will be used to circumvent the reactor and send reactant gases to the mass spectrometer to record the composition of the gas mixture. A leak valve will be used to reduce the gas pressure prior to entering the mass spectrometer.

Sensors such as the thermocouple and pressure gauge will be used to log the temperature and pressure at different locations in the system. For simplicity, the temperature of the reactor wall will be assumed to be the temperature of the catalyst when performing experiments. A water bubbler was added to the system to test running water vapor through the system.

Mass flow controllers (MFCs) will be used to control the mass flow rates of the system and the total system pressure. Dalton's Law states that the total pressure in a mixture of nonreacting gases is equal to the sum of the partial pressures of the individual gases [4], so the total system pressure will be dictated by the pressures of the gases released upstream of the MFCs.

The gases will converge into a main gas line via a four-way connector, where they will then be preheated with a rope heater. The preheating of the gases will improve the efficiency of the system by reducing the heat transfer taking place in the reaction chamber to bring the temperature of the catalyst and gases to thermal equilibrium. The catalyst will be independently heating via a heating jacket that will be wrapped around the flow reactor. The gas lines upstream of the reactor will also be wrapped in insulation to avoid heat loss, while the line downstream of the reactor will be unwrapped to allow the gases to quickly cool before reaching the exhaust or mass spectrometer.

Flow Reactor Design

The flow reactor design is shown in **Figure 6** (p.8) . The high temperatures and pressures used in the flow reactor were taken into large consideration when generating this design as a safety precaution.
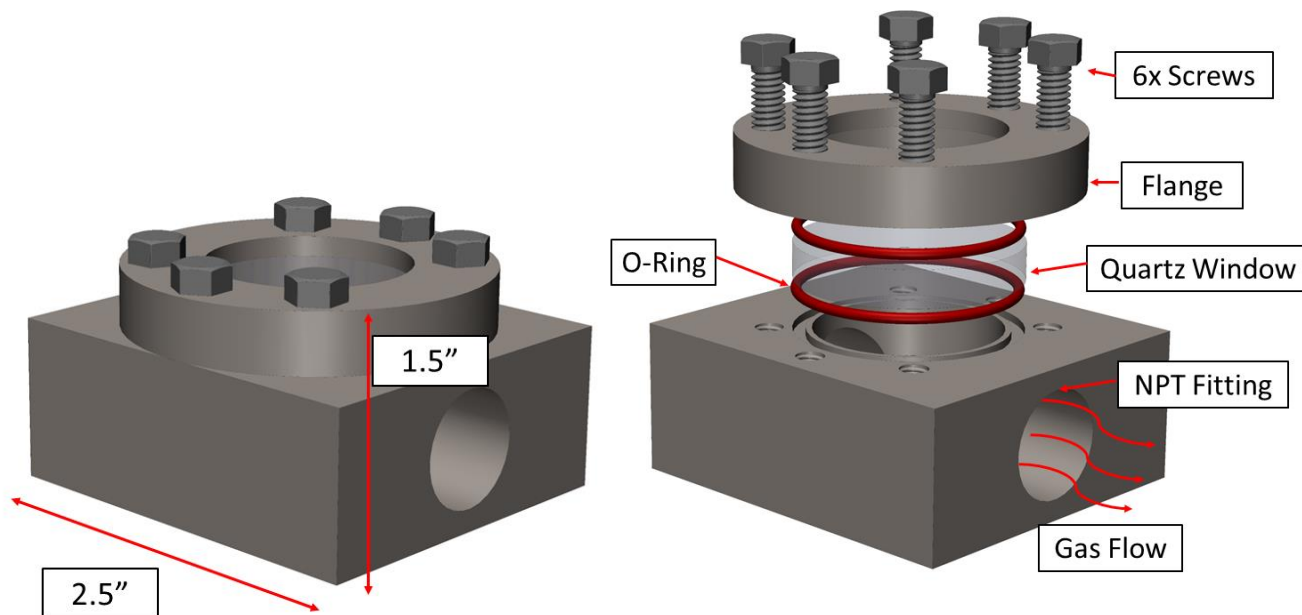
Figure 6: Flow reactor design. The flow reactor materials were selected based on their compatibility with the temperatures, pressures, and chemicals that will be used in this process.

The size of the flow reactor is significantly smaller than the one currently used in the batch reactor. The more compact size of the flow reactor is estimated to reduce the dead volume by at least 82%, which will enhance the efficiency and accuracy of the reactions run through the new system. Additionally, the NPT fittings on the sides of the reactor enable a more modular design so that the reactor can be disconnected from the system and replaced if necessary.

A flange was designed for the window to load and unload the catalyst from the top of the reactor. This flange also allows for greater reactor modularity since the window can be easily replaced if it breaks. The window flange will be sealed using two O-rings to prevent leaks and evenly distribute the forces acting on the class from the system pressure. The *Parker O-Ring Handbook*, the industry standard, was used to determine the optimum O-Ring groove design. The flange will be secured to the reactor body by using a torque wrench – this will prevent over-tightening or uneven loading of the glass, which may cause it to break.

The body of the reactor will be made from 316 Stainless Steel due to its strength and chemical compatibility with the gases that will flow through the system. The window will be made of quartz due to its wide transmission range (200 μm – >2000 μm) and ability to withstand the high system pressures. A kalrez O-ring will be used due to its ability to withstand high temperatures and due to its chemical compatibility with ammonia.

Flow Reactor Gas Flow Considerations

The flow of gases through the reactor was a concern when designing the flow reactor due to its potential to flow around the catalyst suspended within the reactor. A simplified Finite-Element-

Analysis (FEA) was conducted in COMSOL to determine the flow path of the gases through the flow reactor with no catalyst present. The streamlines of the gases are shown in **Figure 7** below, while **Figure 8** shows the velocity profile of the gases.
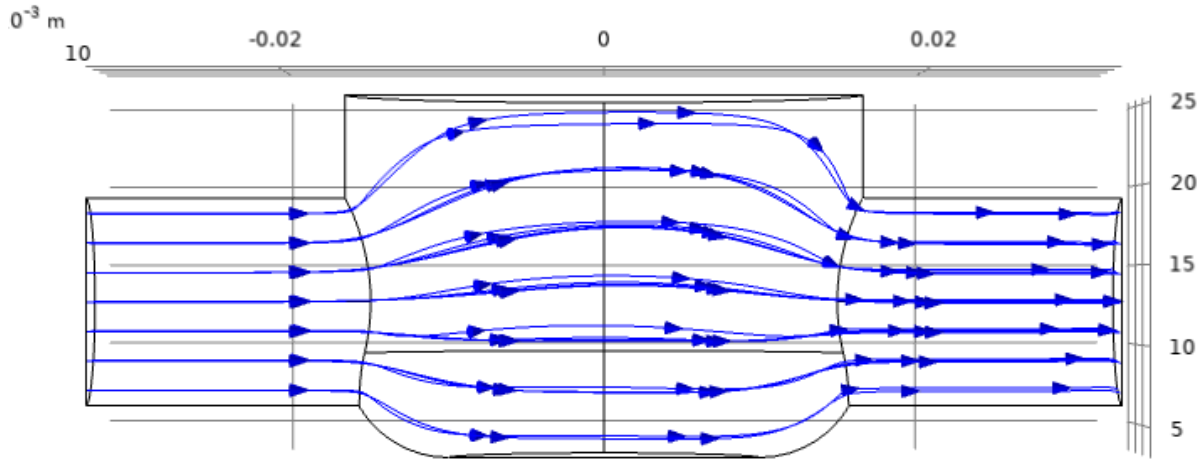

Figure 7: COMSOL gas streamlines within the reactor design. The addition of a fillet on the bottom of the reactor smooths the streamlines and prevents the potential for turbulent regions in the corners of the reactor.

The COMSOL streamline simulation illustrated how the addition of a fillet to the bottom of the reactor surface smoothed the streamlines and minimized the potentially turbulent regions within the reactor. To ensure that the small, powdery catalyst does not stick to regions will no streamlines, a transparent mesh support will be added inside of the reactor.
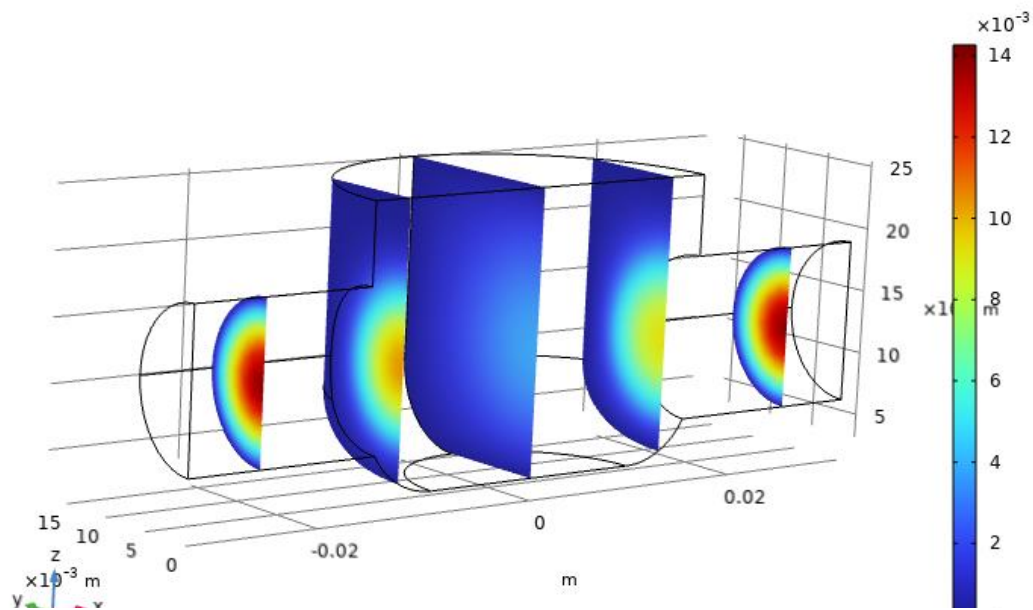

Figure 8: COMSOL velocity distribution within the reactor. The velocity distribution in the middle of the reactor is diffuse, with a slightly larger concentration in the center, where the reactor will be placed.

The velocity distribution shown in **Figure 8** above confirms the diffuse velocity profile in the middle of the chamber. The similar inlet and outlet velocity profiles indicate that the changing geometry in the middle of the reactor will not generate turbulent flow conditions in the reactor, which would move the catalyst to undesirable places inside. The velocity profile is slightly more concentrated in the center of the reactor, which is where the catalyst will be placed. This velocity profile indicates that the internal reactor geometry is sufficient to use for the flow reactor.

DISCUSSION

The flow reactor system and flow reactor design are in the process of being finalized, and building will commence early next year.

Additional design considerations have been added to the flow reactor design – a method is currently being developed to load and unload the catalyst in an easier manner than through the window. A threaded opening will be added to the side or bottom of the catalyst, and the design will be 3D printed to test loading and unloading the catalyst before the part is sent to be manufactured.

The design presented in this capstone report will only be the first iteration of a flow reactor for ammonia synthesis. Future iterations of the design will include two windows in the flow reactor to allow for in-situ Fourier-Transform Infrared Spectroscopy (FTIR). Programmable Heating and Quenching (PHQ) [5] may also be used in the future to precisely control the heating of the catalyst within the chamber.

CONCLUSION

The presented flow reactor design addressed the limitations of the batch reactor and will enable easier testing of different temperature, pressure, and catalyst combinations for ammonia synthesis. This design will open the path to create continuous flow photoreactors that are suitable for industrial use, thereby paving the way for green fertilizer production to be implemented on a larger scale. The results of this project are far-reaching; it will enable more sustainable and equitable access to fertilizer, as well as fight the climate crisis, whose effects are already palpable and hitting more vulnerable communities the most severely.

References

[1] "Current World Population." *Worldometer*, https://www.worldometers.info/world-population/.

[2] Lim, J., Fernández, C. A., Lee, S. W., & Hatzell, M. C. (2021). Ammonia and Nitric Acid Demands for Fertilizer Use in 2050. *ACS Energy Letters*, 6(10), 3676–3685. https://doi.org/10.1021/acsenergylett.1c01614

[3] Liu, Xinyu et. al. "Life Cycle Energy Use and Greenhouse Gas Emissions of Ammonia Production from Renewable Resources and Industrial By-Products." Green Chemistry : An International Journal and Green Chemistry Resource : GC, vol. 22, no. 17, Cambridge: Royal Society of Chemistry, pp. 5751–61, doi:10.1039/d0gc02301a.

[4] Silberberg, Martin S. (2009). *Chemistry: the molecular nature of matter and change* (5th ed.). Boston: McGraw-Hill. p. 206. ISBN 9780073048598.

[5] Dong, Qi et. al. "Programmable Heating and Quenching for Efficient Thermochemical Synthesis." Nature (London), vol. 605, no. 7910, England: Nature Publishing Group, pp. 470–76, doi:10.1038/s41586-022-04568-6.