University Turbine Systems Research (UTSR)

2018 Gas Turbine Industrial Fellowship Program

Carbon Capture Technology

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1. Introduction

The Gas Technology Institute (GTI) is a leading non-profit research, development, and training organization that is devoted to addressing global energy and environment challenges. For more than 75 years, GTI has been striving to enable a secure, abundant, and affordable energy future through the development of technology-based solutions for industry, government, and consumers.

The research initiatives at GTI span the energy markets value chain encompassing supply, delivery, and end use. Ready to take on the future of energy demands, GTI not only does research with conventional natural gas, but also with hydrogen, carbon management, renewable energy, and unconventional oil and gas. With a clear record of success, to date, GTI programs have resulted in nearly 500 products, 750 licenses and more than 1,300 associated patents.[1]

With growing concerns for climate change, there is a call to either reduce the amount of nonrenewable energy used, or to make the use of nonrenewable energy "green" and more efficient. Reaching 400 ppm, carbon dioxide is the main greenhouse gas that is leading to climate change.[2] Industry is responsible for approximately 40% of greenhouse gasses, and for such reasons is being called to take action in many countries to eliminate carbon emissions.[2] Options to reduce and eliminate carbon emissions include post or pre-combustion capture, electrochemical separation, or oxyfuel combustion. Throughout the summer, my projects focused on improvements and research involving post-combustion carbon capture. Post-combustion carbon capture is considered the most economical method of carbon capture and has been used for over 60 years.

2. Rotating Packed Bed Reactors

2.1 Introduction

Post-combustion carbon capture is considered to be the most straightforward carbon capture process for existing industrial facilities. The Gas Technology Institute and Carbon Clean Solutions Limited (CCSL) have partnered up with the help of funding from the Department of Energy with the goal of taking a breakthrough technology used to capture carbon closer to commercialization.[3] This novel technology (entitled "ROTA-CAP") utilizes rotating packed bed reactors (RPBs) to intensify the process of post-combustion carbon capture.

2.2 Background

Adsorption towers are often used in coal and natural gas powerplants to remove carbon dioxide from flue gas. Adsorption towers operate following the principles of Henry's Law (eq. 1). Henry's Law states that the solubility of a gas in a liquid is proportional to the pressure of a gas over a solution.[4] CO_2 is absorbed under a higher pressure and low temperature.[4] Desorption (or release) of CO_2 occurs at a high temperature and reduced pressure.[4]

$$(eq.1) \quad P_a = Hx_a$$
$$P_a - partial\ pressure\ of\ component\ a$$
$$H - Henry's\ Law\ constant$$
$$x_a - partial\ pressure\ of\ liquid\ component\ a$$

The most common adsorption processes consist of an absorber and desorber. In the absorber, flue gas containing CO_2 enters the bottom of a packed bed absorber. A lean absorbent (often an amine solvent) flows from the top of the column causing countercurrent contact. Carbon dioxide is absorbed into the amine solution. In the chemical process of adsorption, carbon dioxide is first transferred from the gas to the liquid surface. From the liquid surface the carbon dioxide is absorbed into the liquid solution. After carbon dioxide contact and absorption, the now rich absorbent is sent to a desorber for desorption. With the addition of heat, desorption liberates carbon dioxide from the amine solvent so that the produced lean solvent can be reused for absorption. In this process the rich solvent is fed through the top of a packed bed reactor, and as it flows through the reactor hot reboiler vapors supply the energy needed for the endothermic reaction of carbon dioxide desorption. The resulting product of pure carbon dioxide can then be collected and stored as desired.

There are many limitations to carbon capture by conventional adsorption and desorption towers. Traditional adsorption towers have a low CO_2 loading capacity that limits efficiency. The units also have many costs related to the large amount of solvent used, and the solvent causes corrosion in the unit that frequently requires maintenance. The solvent must also often be replaced as it degrades quickly due to the presence of SO_2, NO_2, and O_2 in the flue gas.[4] Much overhead cost is associated with the high energy consumption during desorption, as it requires heat, as well as with the cost of building the large towers used for the process.

One technology that boast improvements to traditional adsorption and desorption columns is Rotating Packed Beds (RPBs). RPBs boast HIGEE technology. This technology replaces the forces of gravity that is used to drive separation in traditional adsorption towers with centrifugal force. With the use of centrifugal force, the adsorption/desorption process is much quicker, and a wider variety of solvents may be used. RPBs also use less than 20% of the packing height, 70% of the solvent, 25% of the water, and 30% of the electricity required by conventional columns. These improvements drastically decrease overhead, operation, and maintenance cost. To prove that this technological development is worthwhile for commercialization and development, the financial goal of the development of ROTA-CAP is to capture 90% of the carbon in a flue gas stream for thirty dollars per tonne. Having a cost efficient and compact means to capture carbon would hasten the commercialization of carbon capture technology.

2.3 Design and Development

2.3.1 Rotating Packed Beds

The focus of the design of the ROTA-CAP was the novel technology of rotating packed beds. The design was developed with the knowledge provided from past in-house work on rotating packed beds, photos provided by Newcastle University in Tyne, England, and a thorough literature review. The rotating beds were designed to be torus in shape (shaped like a doughnut). The apparatus was designed so that the solvent would be sprayed from the center of the doughnut as the apparatus spins. The centrifugal force due to the spinning would force the liquid through the packing. Exiting solvent would be collected in a containment vessel attached to the rotating unit and sent to the desorption unit. The flue gas (gas containing the carbon to be adsorbed) was to be introduced from the outer edge of the packed bed. Due to an imposed pressure gradient, the gas would be forced to flow countercurrently past the liquid solvent and packing to exit the unit out of a shaft parallel to the motor. The countercurrent flow allows adsorption of the CO_2 into the amine solvent. The “clean” flue gas exiting the unit would be scrubbed with water to remove any traces of amine solvent before it is released into the atmosphere.

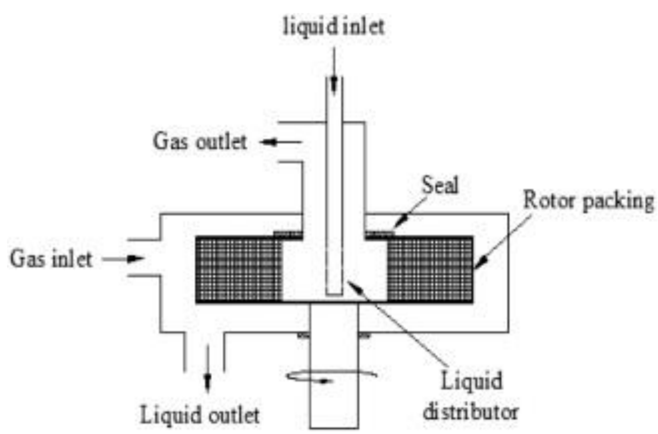

Figure 1. The basic design of the rotating packed be reactor.[5]

Rich solvent containing the captured carbon dioxide would be sent to an RPB used for desorption. The desorption RPB operates in a similar manner as the absorption RPB used to separate the carbon dioxide from the flue gas. A difference is that a reboiler is used to supply hot vapors carrying heat to the RPB. The heat supplies the energy needed to break the bonds formed between the carbon dioxide and solvent. The released carbon dioxide is then collected and stored or processed into other products as desired. The solvent, which is not considered lean (not containing carbon dioxide), is reused in the absorption process.

2.3.2 Solvent

In order to capture carbon via adsorption, solvents must be employed. The most commonly used solvents are amines or salts. Amines for carbon capture provide a quick reaction for adsorption, and require minimal, small equipment (which leads to less overhead costs). Much energy must be supplied in the form of heat to break the bond that forms between carbon dioxide and the amine during desorption. More concentrated amine solvents capture more carbon dioxide but are also more viscous (which causes issue in traditional, gravity driven adsorption towers). Salts are advantageous in that they form a weak bond with carbon that is easily broken, meaning that little energy is needed for desorption. During the adsorption portion of the process, it is advantageous to keep the solvent cool, as the cooler the solvent the more carbon dioxide it can capture. If more carbon dioxide can be captured per amount of solvent used, the process is more efficient. For that reason, the process was designed to have intercooling drums and heat exchangers to keep the solvent used in adsorption as cool as possible. The proprietary solvent to be used in the ROTA-CAP apparatus was developed by Carbon Clean Solutions for improved carbon capture.

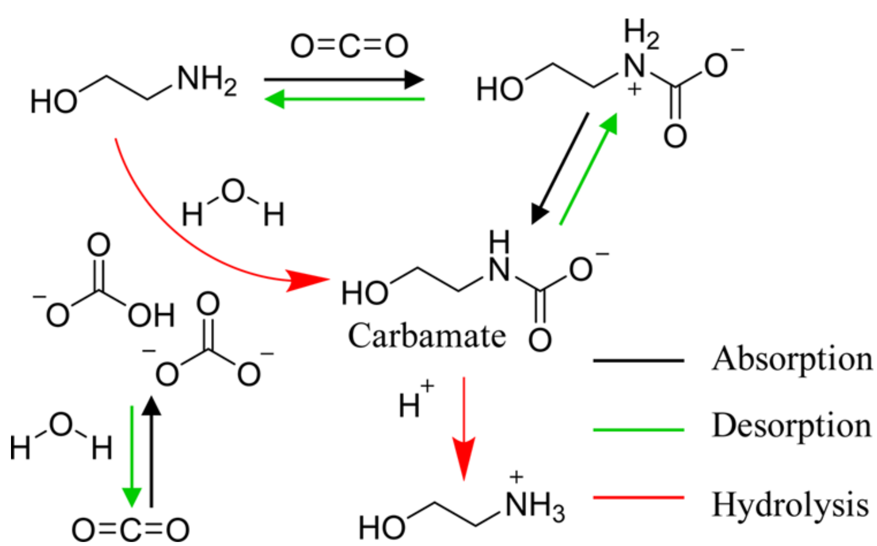

Figure 2: Reaction of typical amine MEA with carbon dioxide for absorption or desorption.[6]

2.3.3 Design Focus

To ensure safety and successful operation, there were several areas of focus in the design of ROTA-CAP. The core units of the system would consist of a rotating absorber and desorber. As depicted in the process flow diagram (PFD) in figure 3, these units will be connected through various piping and have a cross-flow heat exchanger in between to "recycle" the solvent and ensure adequate solvent temperature. A reboiler is connected to the desorber and supplies the heat necessary to break the bonds formed between the solvent and carbon dioxide.

The PFD depicted in figure 3 shows a simplified depiction of the flow and equipment to be used in the process. It serves as a basis for more complex Process and Instrumentation Diagrams (P&IDs). P&IDs depict every major and minor flow, piece of equipment, valve, and instrument employed. Being so detailed, these diagrams are used to construct the unit and account for the various parts.

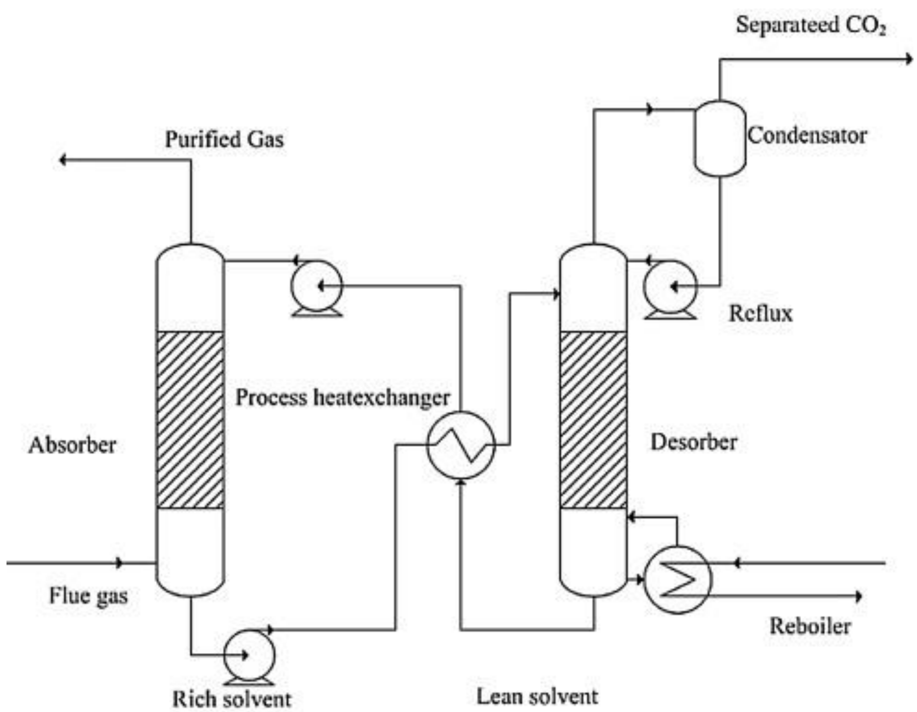

Figure 3. A simplified PFD for a traditional carbon capture system. In the ROTA-CAP system the traditional absorber and desorber will be replaced with RPBs.[7]

In terms of units on the ROTA-CAP system, focus was placed on the development of the rotating packed beds (RPBs). Being sized at approximately 3 feet in diameter and several hundred pounds, it was critical to ensure the RPBs were designed adequately to prevent injury and ensure successful operation.

One critical area of design dealt with balance of the RPBs. The RPBs will rotate at speeds ranging from 400-1000 RPM. At such high speeds it is vital to have an even distribution of weight in the apparatus or one risks damaging the motor and unideal operation. To ensure even solvent distribution in the unit, the solvent will be sprayed from the center of the unit outward via several nozzle with different orientations. To monitor the weight distribution in operation, vibration sensors will be attached throughout the RPBs. If weight maldistribution is detected operations will be stopped and the unit will be adjusted.

Figure 4. Produced rotating packed bed reactors and interior packing (Newcastle University)

Considering the size, weight, and mobile nature of the rotating packed beds, it was imperative to choose the correct material to construct the RPBs and the RPBs shell. Rupture of the units would not only damage the equipment and skid, but could also have the potential to hurt personnel. The shell needed to be strong enough to endure the force of rotation while containing a mobile solvent. Due to the flowing solvent, the RPBs also needed to be made of a material that is resistant to corrosion. With those specifications in mind, pressure rated ASME stainless steel was chosen to be the material of construction for the RBPs and the RPB shells. Stainless steel is resistant to corrosion and maintains its strength at high temperatures. Aside from being resistant, stainless steel is easily maintained and requires little maintenance. Possessing strength and resistance to what may be considered harsh conditions, stainless steel will also serve as the material of construction for the majority of the piping and equipment found in the system.

Another important design consideration dealt with the separation of the liquid and gas streams flowing through the RPBs. If the liquid and gas streams mixed at an undesired location, it would prevent adequate adsorption as countercurrent flow would not be possible. To ensure correct separation, adequate seals needed to be designed that could withstand high rotation and ensure the separation of the liquid and gas streams. To ensure proper construction, a knowledgeable engineering firm was consulted to determine the best option for ROTA-CAP.

2.4 Calculations

Calculations were completed to estimate various flowrates throughout the system. One such calculation was to determine the volumetric flowrate of the cooling water through the heat exchangers. Cooling water was used to keep the solvent cool and ensure the unit operated efficiently. Cooling water flowrate calculations were completed using the energy transfer equation (equation 2). All variables were known except mass flow rate (of the cooling water) which was calculated.

$$(eq.2) \quad Q = mc\Delta T$$

$$Q - heat\ duty\ \left(\frac{MBtu}{hr}\right)$$

$$m - mass\ flow\ rate(\frac{lbm}{hr})$$

$$c - heat\ capicity\ (\frac{Btu}{lbm * \circ F})$$

$$T - Temperature\ (\circ F)$$

To calculate the volumetric flow rate (of the cooling water), the mass flow rate was divided by the density of water, as shown in equation 3.

$$(eq. 3) \quad v = \frac{m}{p}$$

$$v - volumetric\ flow\ rate\ (\frac{gal}{min})$$

$$m - mass\ flow\ rate\ (\frac{lbm}{hr})$$

$$p = density\ (\frac{lbm}{gal})$$

2.5 Safety Considerations

Safety considerations are key in the development of new operations to prevent hazardous conditions, property destruction, or injury. Many safety factors were considered in the development of ROTO-CAP. In analyzing safety, several Hazard and Operation Studies (HAZOPs) were conducted. A HAZOP is a structured, systematic examination of a process or operation that is used to identify and evaluate problems that may pose risks to personnel or equipment.

In a HAZOP the process being analyzed, as depicted in a process flow diagram, is divided into nodes for analysis. During analysis of each node, one assumes that processes nodes before and after the node being analyzed are operating correctly. Although the equipment in the surrounding nodes is assumed to be working properly, the problems arising in the node being analyzed may have consequences that affect the surrounding nodes. One also assumes that there are no safety measures in place to prevent the worst-case scenario from arising. Issues such as high/low temperature, pressure, flow, rupture, contaminants, are then discussed and analyzed.

During a HAZOP, the most important elements to consider are severity and frequency. Rankings for severity and frequency are given to each of the discussed issues based on the effects the problem would have on personnel, community, environment, site, or operability.

Rankings for severity are made on a scale of 1 to 4. A ranking of 4 would mean that the severity of the incident is major. Personnel may be killed or permanently disabled. Offsite illness, injury, or damage would also be found in the community. Environmentally, there would be significant release with major offsite impact and permit violation. The site would also face major or total destruction to process area(s) at a cost of $1,000,000. The operability of the project would be severely damaged resulting in a delay greater than 1 month.

A ranking of 3 for severity indicates serious impact. Personnel would be found to have one or more severe injuries. The community would have various complaints regarding odor and noise. Environmentally, there would be a release with minor offsite impact and/or a permit violation. Process areas would face minor damage at a cost less than $100,000. Regarding operability, sever damage to facility and equipment would result in a few weeks delay to the project.

A severity ranking of 2 indicates minor impact. Personnel would face minor injury and lost time. The community would likely have minor noise and odor complaints. With regards to environmental issues, there would be release to the environment which results in agency notification or permit exceedance but not off-site impact. Some damage to equipment would be present and cost greater than $10,000. There would be minor damage to the facility and such damage could be repaired within several days.

A severity ranking of 1 is incidental. Personnel would have minor injury and no lost time. The issue poses no injury, hazard, or annoyance to the public. Environmentally, it would be a site recordable event with no agency notification or permit exceedance. Minimal site damage would be present costing less than or equal to $10,000. Operations could be resumed within a shift of the event.

Frequency rankings were also assigned on a scale of 1-4. A ranking of unlikely (1) indicates a chance of occurring during the project life. Seldom (2) indicated a change of the issue occurring monthly. Occasional (3) issues may occur on a weekly basis, and frequent (4) issues may occur every day.

The total risk ranking was then found by multiplying the severity by the frequency for each issue. The ranking ranged from 1 to 16. Rankings of 12-16 are considered unacceptable and must be corrected before proceeding. Rankings of 8-11 need to be corrected and operations may continue only if safeguards are in place. A rank of 4-7 warrant investigation, safeguards need to be put in place before operations. Rankings of 1-3 are not serious and only need to be corrected if economical.

Two HAZOPs have been completed for the ROTA-CAP system. 169 recommendations have been identified and are being considered as the design process continues.

Severity of Incident	Frequent (4)	Occasional (3)	Seldom (2)	Unlikely (1)
Major (4)	16	12	8	4
Serious (3)	12	9	6	3
Minor (2)	8	6	4	2
Incidental (1)	4	3	2	1

Table 1. This chart depicts the risk ranking matrix based on severity and frequency.

2.6 Future Work

Work on ROTO-CAP will continue well into 2020. At this point, designs are nearly completed, and many pieces of equipment and instrumentation have been ordered. A skid has been designed and purchased. The system will be built on the skid from September to October 2019. The unit will be tested at GTI from November 2019 to January 2020. The unit will then be prepped to ship to the National Carbon Capture Center (NCCC) in April 2020, and NCCC testing of the unit will begin in July of 2020. Throughout testing of the apparatus, variables that will be tested include (1) Rotating packed bed rotational speed 400–1000 RPM, (2) Absorber Liquid/Gas ratio 0.5–5.0 kg/m3, (3) Solvent circulation rate 30–150 kg/h, (4) Solvent concentration/viscosity 40–80 wt.% (5–100 cP), (5) Desorption unit operating pressure/temperature 0.0–1.0 bar(g) (100–130°C) (6) Flue gas composition (synthetic, natural gas-fired, coal-fired). Through research and testing of those variables the system will be optimized with hopes of capturing carbon for $30 per tonne or less.

3. GO-PEEK Post Combustion CO2 Capture

3.1 Introduction and background

3.1.1 Membranes

Membranes are selective barriers that allow some substances to permeate (or pass through) but stop others. Using the selective nature of membranes, they can be used to capture carbon. Membranes selectivity results from the nature of the design or composition of the membrane. The GO-PEEK membrane system utilizes polyether ether ketone (PEEK) and Graphene Oxide (GO) membranes. PEEK is considered to be one of the "best" commercial plastics, as it has superior thermo-mechanical properties and chemical resistance. The superior properties of PEEK are a result of the semi-crystalline nature of the polymer. PEEK membranes have been developed and used by GTI at the National Carbon Capture Center (NCCC). They have been found to remove greater than 90% of CO2 with a mass transfer coefficient of 2.0 (sec)-1, which exceeded the goal mass transfer coefficient of 1.7 (sec)-1.

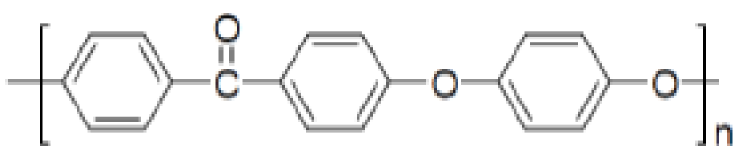

Figure 5. Chemical structure of PEEK

Polymer	Tensile modulus (GPa)	Tensile strength (MPa/kpsi)	Max service temperature (°C/°F)
Teflon™	0.4-0.5	17-21/2.5-3.0	250/480
PVDF	0.8	48/7.0	150/302
Polysulfone	2.6	70/10.2	160/320
PEEK	4	97/14.1	271/520

Table 2. Comparison of physical properties of several commercial plastics.

GO membranes are composed of graphene oxide, which is a graphene derivative. GO membranes are considered a "perfect" material for use in membranes due to their "mono-atomic thickness, 2D structure, high aspect ratio, good mechanical strength, chemical inertness and thermal stability".[8] Studies indicate that GO is also more highly selective for carbon dioxide permeation compared to any other gas.[8]

3.2 GO-PEEK System

The GO-PEEK post combustion CO_2 capture system works by combining the use of both Polyether ether ketone (PEEK) and Graphene Oxide (GO) membranes. Besides being composed of different components, these membranes differ in the driving force behind mass transport and permeation. The driving force for the PEEK membrane is the solvent Methyl diethanolamine (MDEA). Much energy is expended in desorption of the solvent (as heat is required). Besides energy cost, there is a large cost associated with solvent replacement due to degradation. The driving force for the GO membrane is pressure. Vacuum pressure is used to pull the permeate and retentate streams through the GO membrane. Energy must then be expended to get the permeated carbon dioxide pressurized for sequestration. Individually, both types of membranes have been found to be successful for uses of carbon capture. The goal of the combination of the membrane systems is to optimize cost. In typical membrane operations, there is a series of membranes in a system. For example, a pilot unit consisting of a series of 4 PEEK membranes has been operated by GTI at the National Carbon Capture Center (NCCC). The bench scale GO-PEEK membrane system will consist of 2 membranes in series, 1st the GO membrane followed by the PEEK membrane. Each membrane is to remove half of the desired carbon dioxide from the gas stream. By combining the GO and PEEK membranes the cost associated with the solvent, solvent desorption, and vacuum pump should work out to be cheaper and more efficient than using a single type of membrane.

3.3 Testing

With an operational unit, shakedown was ready to begin. Various leak tests were performed, flow meter flow rates were confirmed, and control meters were tested and calibrated. Once the unit was checked thoroughly for any abnormalities, the GO Peek membrane was installed. The GO membrane required special care, as it degraded upon becoming dry or wet. The membrane was stored in a humid environment and installed on the skid before testing and removed for storage after testing. To ensure an adequate amount of humidity in the system before the membrane was attached, a humidifier in the system was heated to approximately 165 degrees. A knockout was present above the humidifier to allow any excess water to drop out of the system. This ensured that the air in the system was saturated but not wet. With adequate humidity in the system, the membrane was attached.

Before testing the combined membrane system, reasonable data needed to be collected for the GO membrane to ensure it was working properly. To see if the GO membrane was operating correctly, samples from the permeate and retentate side of the membrane were analyzed in a gas chromatographer. By analyzing the gas chromatography peaks the presence and concentration of carbon dioxide was determined. As stated earlier, approximately 50% of the carbon dioxide needed to be removed by the GO membrane. After extensive testing, it was found that carbon dioxide was not being removed, as the permeate steam was not being pulled through the membrane. The membrane was faulty and more GO membranes were ordered.

While waiting for the membranes to arrive, troubleshooting was completed to determine operational adjustments that could prevent further issues. One change was made regarding unit temperature. Previously, temperature throughout the unit was only loosely monitored to ensure the temperature in the humidifier was near 165 degrees Fahrenheit. With minimal monitoring it was possible that the piping leading to the membrane was at too low of a temperature. Being at too low of a temperature, water may have condensed out of the humid gas into the piping. Condensation in the piping would cause pulsing, inconsistent flow (which was observed in testing with a bubble flow meter). With a buildup of condensation, water could flow into and damage the GO membrane. To prevent condensation changes were made to operations. The humidifier was kept at 165 degrees Fahrenheit, the knockout above the humidifier was kept hotter than the humidifier (at 185 degrees Fahrenheit), and the membrane (with heat wrap) was kept at 175 degrees Fahrenheit. By keeping the temperatures past the humidifier greater than the humidifier temperature, condensation of the saturated gas would be prevented. Startup conditions were modified so that the membrane was not attached to the apparatus until all temperature specifications were satisfied.

Upon receiving new GO membranes, the unit was tested with the new operating conditions. Two membranes were tested, both of which yielded unsuccessful results. Neither membrane was found to have a selectivity for carbon dioxide, which should have been the only component present in the permeate stream. The permeate stream was found to have the same carbon dioxide composition as that input flow to the membrane. Further testing was done on each membrane. On one of the new membranes, leakage was observed through both sides of the tube. This indicated a broken fiber in the membrane. For the other membrane, there was a leak on one side. This indicated the membrane seal was bad.

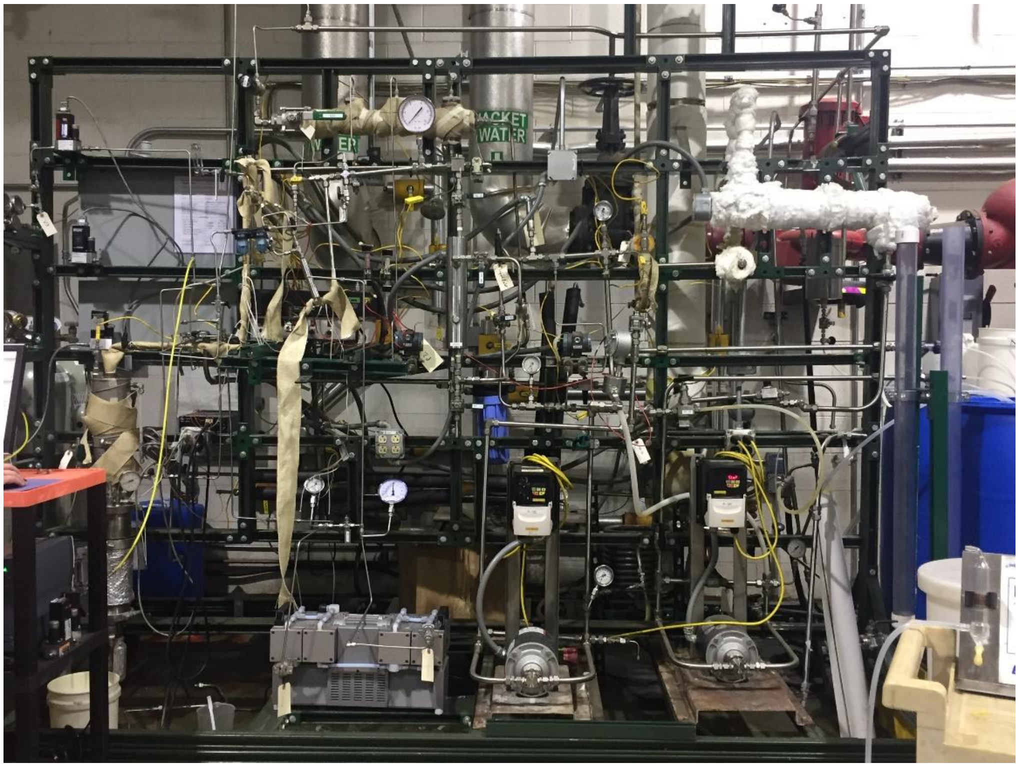

Figure 6. GO-PEEK membrane apparatus.

3.4 Future Work

Thus far, various issues with the membrane system have limited data collection. Faulty membranes and system issues have stunted progress. Future work includes troubleshooting further problems with the membranes or system, collecting reasonable data for permeate/retentate flow through the GO membrane, and then getting the entire system operational with the combined GO- PEEK membrane system. Such operational success will be the basis of determining if the GO-PEEK membrane system is more efficient than a single type membrane system.

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