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Amino-polymer for CO₂ Capture by Vacuum Swing Adsorption

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Amino-polymer for CO₂ Capture by Vacuum Swing Adsorption

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Honors Research Project

Submitted to

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Abstract

Carbon Dioxide (CO₂) acquisition currently relies on processes that capture it from the exhaust of flue pipes from factories or other industrial processes. However, systems that capture it from the standard atmosphere in high amounts and concentrations are tools being heavily worked upon to clean the excess amounts left in the air. The applications of sorbent compounds in conjunction with amines and other additives is an innovative method at combating CO₂ pollution. An ideal solution would use an amine sorbent to trap the high levels of absorbed CO₂ with a low binding energy (less than 45 kJ/mol) and subsequently release them into a stored vessel at ambient temperature with a vacuum swing adsorption system. Attempts at finding a best mixture will be conducted through utilization of the system, utilizing a bed syringe containing the sorbent mix and a vacuum syringe to pull on and subsequently release the CO₂ into a measuring apparatus. Methods of data analysis including Infrared (IR) spectroscopy, CO₂ concentration analyzers, volume expansion, and liquid bubbling will be the primary methods focused on quantifying and investigating such a composition. The main goal of this project is to find a best combination of sorbent and chemicals to contain and release CO₂, with a secondary objective of determining a best method of analysis for further research into the subject matter.

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Executive Summary

Statement of the Problem

CO₂ capture systems are built largely with the focus of capturing emissions from industrial processes. A large majority of these processes being developed focus on the utilization of a solvent absorbing exhaust CO₂ within an absorber column, then applying a heat source to remove it and recycle the solution. However, the heat applications of the process result in lost efficiency, requiring energy from the process to sustain it. Additionally, most systems only focus on direct point contact of emission, unable to address the CO₂ that has escaped into the atmosphere [1, 7, 9]. With continual rises in pollution worldwide based on multitudes of origins [8], more advanced and competent systems are continually under development.

That being said, a number of technologies are under work on capturing CO₂ in air, though most of them still rely on heat as a source of its removal from a sorbent. The method of analysis emphasized in this report uses a vacuum swing arrangement with sorbent compounds actuating CO₂ capture and its controlled containment for purity and heuristic analysis through a variety of methods. The apparatus has been constructed in conjuncture with the Chuang FirstEnergy Research Group and their ongoing research of atmospheric CO₂ capture [2].

Statements of Quantitative Results

Several data sets were collected, some of which focused on optimization of a best sorbent to use in the system and the others on the efficacy on measurement systems. The results for the sorbent are shown in comparison with one another in tandem with results from varying analyses used. The IR spectroscopy analysis show the CO₂ bonding curve on a graph overtime to indicate rate of CO₂ released by the system. CO₂ analyzer data would come by means of current analysis of CO₂ detected over time, with peaks indicating severity of CO₂ lost and the flatline as the basis of air flow detected. Volumetric tests indicate amount of air and CO₂ collectively captured by the system, with the ability to confirm how much gas existed within the system. The data sets could then be compounded and compared to find potential trends between them to properly assess amount of CO₂ capture by the system and amine assessed. All these tests would be conducted on a base sample for comparing multiple times to assure data is accurate with the best method utilized for examination of varying the sample analysed. Analysis then focalized on the best sorbent for usage under three fields of grouping: TPSENa, ASPEN, and Polyurethane (PU).

Conclusions

Data interpretation and conclusions came most easily through the IR spectroscopy method with its high fidelity for minutiae in the samples. While CO₂ analyzer and Volumetric tests help determine trends and amounts of CO₂ released, they do not aid in fully understanding pure amounts of CO₂ indicated and require high levels of experience to understand what is being detected by the system. The DRIFT IR proves most beneficial in this respect, as it both indicates flow of CO₂ and additional compounds going past the cell. Its usage in tandem with the volumetric tests results in the knowledge of both what is being pulled from the system and how much CO₂ there is.

Across all sample types, the TPSENa sorbent proved to have the highest capacity for containing CO₂ and the easiest release of it into a storage container. The ASPEN and PU perform admirably, however underperform in comparison to TPSENa. Additionally, the ability to adjust TPSENa with ease with other amines, surfactants, or solvents further promote it as the best in its modifiability.

Broader Implications

The study indicates investigation into other methods of CO₂ analysis by means of spectroscopy. A method already being worked upon is the application of mass spectroscopy, an equally complex method of analysis like a DRIFT IR but could compound upon and verify one another's results. A more in-depth discussion on the modifications of the TPSENa could equally work as a basis of study for polymer research with investigations into the roles of water affinity and dielectric effects.

Recommendations for Future Work

A larger range of sorbent types tested for a general base of comparison would aid the confirmation of a best case to adjust and meet maximum efficacy possible by such a method. Analysis methods at this point are extremely reliable with most doubts on data deriving from the vacuum swing itself, not so much on the analysis method in use.

Introduction

Advancements in industry often correlate to higher levels of negative emissions from processes. Within the fields of chemistry and biology, the most notable exhaust is CO₂. Methods of combating the flow directly from plants have been instated for some time now, with a good number focusing on the utility of amine-based compounds to bind CO₂ in solution [7]. Efficiency and purity of potential sorbents containing amines is an important part of advancements both for capture and for utility in all systems. However, the analysis and conclusions to decide on a best option is also required, needing multiple systems to be investigated to find a best choice for continuous use. The goal of this project is two parts: investigating the best method of analysis of CO₂ captured and the analysis of varying sorbent compounds to find a best version [1, 6].

Background

The work done throughout this report was done in conjuncture with and building off work in the FirstEnergy Research Group. The overall project itself is encouraged by the Department of Energy to focus on different and new ways to capture CO₂, with the one investigated in this report of primary concern. Amine based capture of atmospheric CO₂ is deemed highly important and effective in both material and energy consumption. For this research, several systems of analysis and amine sorbents were tested and synthesized. The three systems tested for compound analysis of CO₂ were a CO₂ analyzer, volumetric testing setup, and IR DRIFT, diffuse reflectance infrared Fourier transform, cell. A variety of sorbents were used throughout testing but will be generalized under the following three groups: TPSENa, ASPEN, and Polyurethane (PU). Each sorbent is comprised of highly differing amines and associated secondary components, the details of some left unknown due to company secrecy. As such, a summary of each group's efficacy will be presented to encompass their shared success and failure [2-5].



Figure 1: Array of general appearance of the sorbents tested, with TPSENa on the left, ASPEN in the middle, and PU on the right.

Experimental Methods

Design and Testing of Apparatus

The system utilized is a vacuum swing dual syringe apparatus. It operates by allowing an inert gas, typically argon, through an entry port with a two-way valve directing the current towards the 50-cc syringe. The 50-cc syringe utilizes 30cc of sorbent material of choice for CO₂ capture with paper material packed into the end of the syringe to prevent dust clogging the system. Gas flows through both exits, the first with the two one-way valves and the other through the 500-cc syringe. Inert gas is run through the system for approximately 20 minutes to ensure any remnant gasses are left over from prior testing. The gas inlet is then transferred from argon to air and is allowed to pass over the sorbent for 5 minutes. After adsorption all valves are switched to restrict gas flow, enabling vacuum to be pulled on the 50-cc syringe by the 500-cc syringe. Depending on the test conducted, the gas inlet is either entirely shutoff or inert gas is allowed through the system for a sensor to operate correctly. For testing purposes of what a pure CO₂ inlet looks like, a testing port is attached near the outlet of the system to enable injection of pure gas. All tests conducted had the 500-cc syringe pull vacuum for 15 seconds before release to standardized data seen by all systems. A visual of the system is shown below in **Figure 2**.

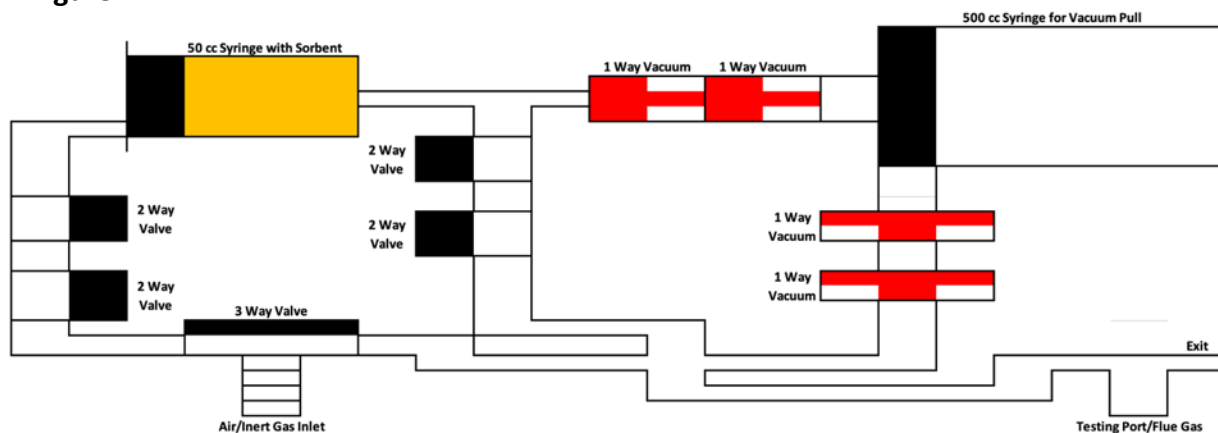


Figure 2: Illustration of the apparatus used for testing.

To test if the system was operating under a vacuum, a simple pressure test across all connections was applied. Wherever tubing or pieces connected by whatever means, soapy water was poured over the area in question. The 500-cc syringe would then draw air until it filled to entirety. All entrances and exits within the system would then be sealed by whatever means available. The 500-cc syringe would then be pushed onto the sealed systems. Points of weakness or failure would begin bubbling indicating further sealing required. Once all leaks are sealed, the apparatus could then be allowed to start testing.

Testing of the sorbents followed an identical protocol for system operation excluding each analysis' specifications. The vacuum swing would be placed in the configuration most suitable for the respected analysis setup with the ending connection attached to the appropriate inlet piping. For the analyzer and IR, the machines would start collecting data with the apparatus attached for 30s to allow a baseline of data collection to be observed. At 30s, the 500cc syringe would pull on the sealed system for 15s, after which it pushed out whatever pulled air from the system it could into the measuring device. There would then be a pause of 15s to allow the system to properly read the gas stream. This 15s pull, push, and 15s wait cycle would be done several times, a minimum of 5 times and upwards to 50 based on the extent of test desired. Based on data obtained, the test could be repeated for assurance of values or in tandem with a secondary system to see how they correlate with one another.

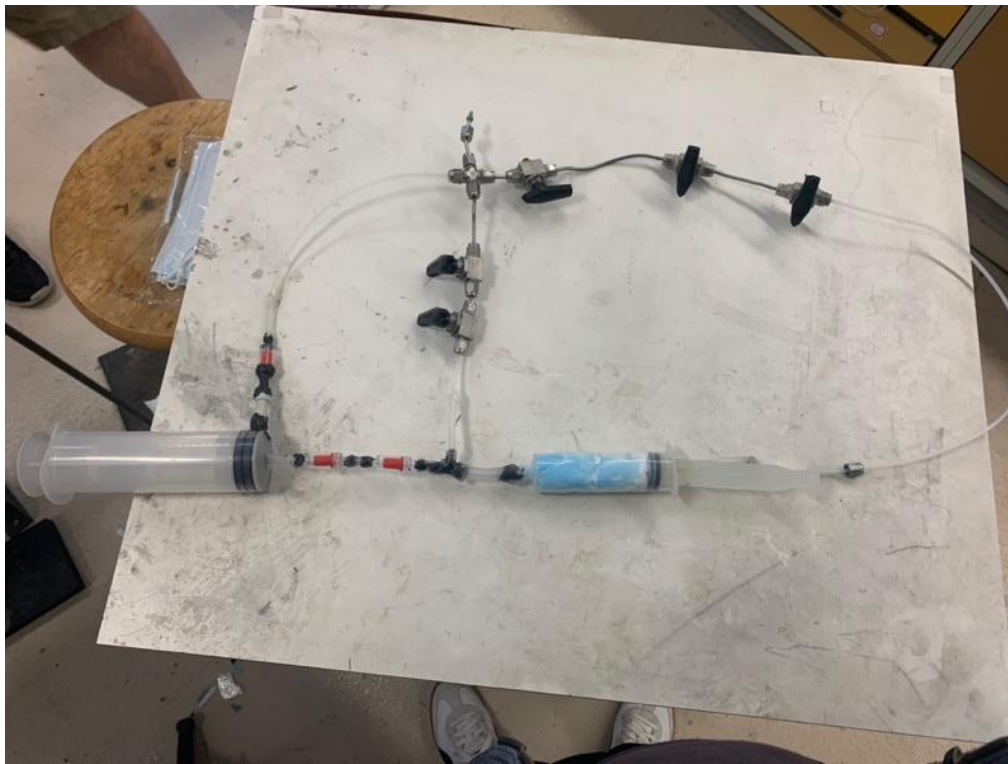


Figure 3: Visual of the apparatus used configured as utilized in all tests.

Sorbents

As stated earlier, three types of amine-based sorbents were used for analysis of efficacy. The primary mixture tested was TPSENa. It comprises of 5.25 g of epoxy resin 825 in 100 g ethanol, which would have 18.75 g of polyethylene glycol (PEG) 200 and 30 g tetraethylenepentamine added. A secondary mixture of 0.5 g of sodium carbonate in 100 g water would be mixed and then added to the main solution, becoming the impregnation solution. This solution would then be added to 50 g of silicon dioxide and dried in an oven at 100°C for 5 minutes and further left to dry in air to avoid killing amines in the final product. Components within the mixture would be interchanged to investigate their varying effects, be it exchanging EPON for P-123 or PEG200 for PPGDA. All mixtures would result in a powdery sorbent that would then be packed into the 50-cc syringe to the 30-cc line ready for use.

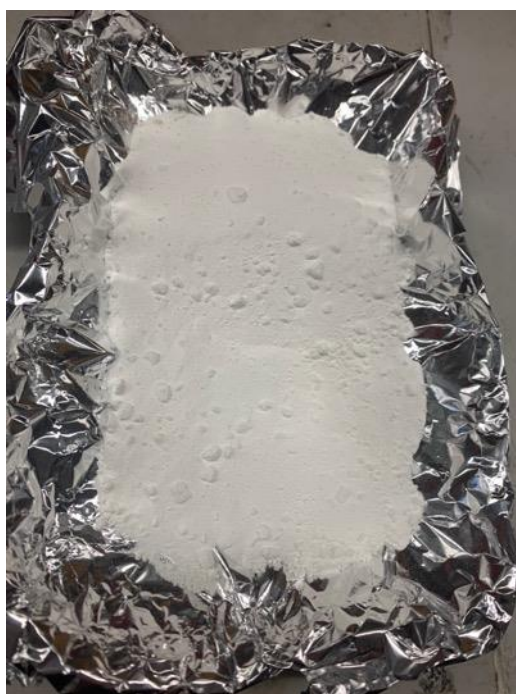


Figure 4: Visual of base TPSENa sorbent.

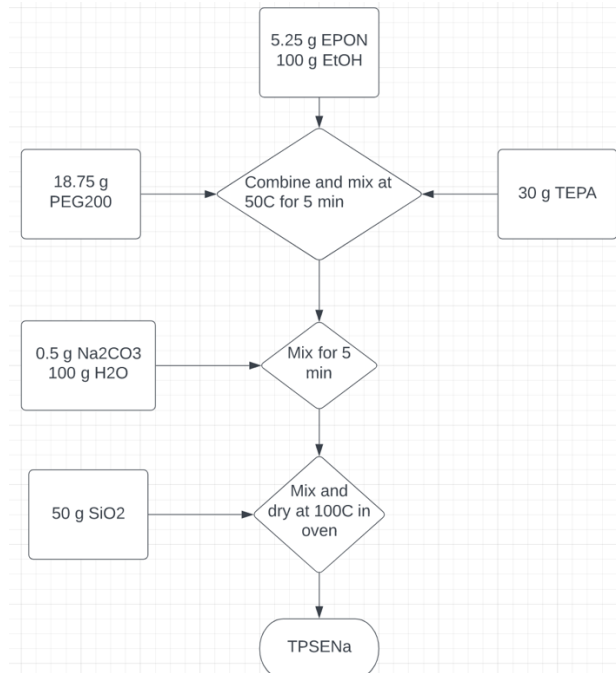


Figure 5: Preparation steps for TPSENa sorbent testing.

The secondary mixtures tested were those from ASPEN. These sorbents were bought from the company in a large variety of mixtures with variable information given. While composition was left obscure, the shape, size, and water affinity of the received compounds came in a range of compositions. The sorbents tended to come either as a powder, chunks, or beads, the latter of which in a variety of diameters to test the potential of bonding surfaces correlating to CO₂ capture. The compound would then come described as either hydrophobic or hydrophilic, a property to keep in mind while testing due to correlation in water weight and CO₂ capture efficiency properties.



Figure 6: Visual of powder (left) and chunk (right) ASPEN sorbents

The final sorbents tested were the PU variants. Tests conducted relied on the Great Stuff brand of PU foam spray [10], which enabled the addition of additives like water, amines, or surfactants to the compounds. The base spray rapidly expands so additions needed to be quickly added and required mass percentages quickly calculated. As such, programs in excel were setup to appropriately find the required masses. These would then be allowed to expand to their maximum volume, after which they would be cut into pieces to be layered into the 50-cc syringe for testing.



Figure 7: Visual of base PU sorbent.

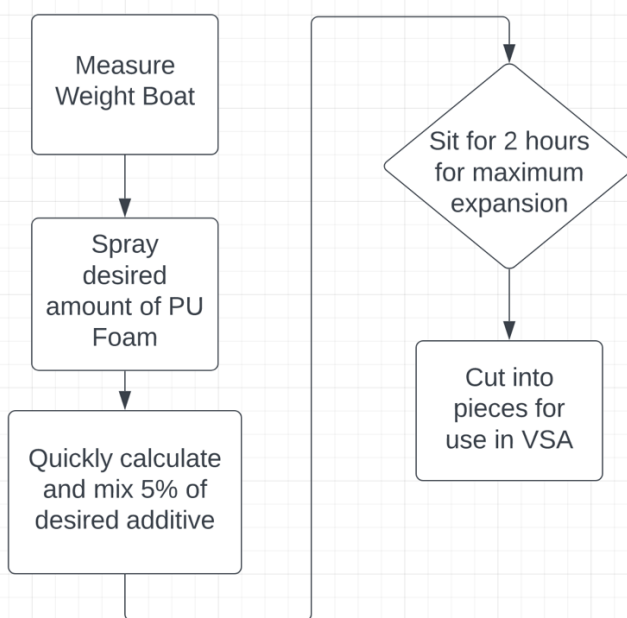


Figure 8: Preparation steps for PU sorbent.

Sample	Composition
TPSENa	28.8% TEPA, 18% PEG, 5% EPON, 0.5%Na, 47,7% SiO2
ASPEN - BMSPA85	Unknown, Silica Aerogel
PU	95% polyurethane, 5% TEPA

Figure 9: Table of sorbent data shown in this paper.

CO₂ Analyzer

The simplest analysis method conducted with the system was its coupling with a CO₂ analyzer, specifically a Guardian Plus configured for CO₂ analyzer. It operates by using a pump to draw air from its inlet line and run it through a CO₂ analyzer recognized as a percent or parts per million. The wiring from the device was rerouted to a laptop to allow data collection via LabView, transforming the percentage to a current value in milliamps over time. This testing setup required inert gas run through the system to prevent error readings from analyzer.



Figure 10: Visual of the CO₂ analyzer with the vacuum swing attached.

Volumetric Test

The middling analysis method was the volumetric testing of the system. It operated by filling a container and 1000 mL graduated cylinder with water. The cylinder would then be placed upside down in the bath enabling tubing to its base. Tubing from the exit of the vacuum swing would run into the graduated cylinder until it reached the top. Analysis of the gas was accomplished by measuring the volume of the liquid displaced by the air. The first vacuum pull would push out all the void space in the system, with the following pulls being pure CO₂. This testing setup did not require inert gas to run through the system.

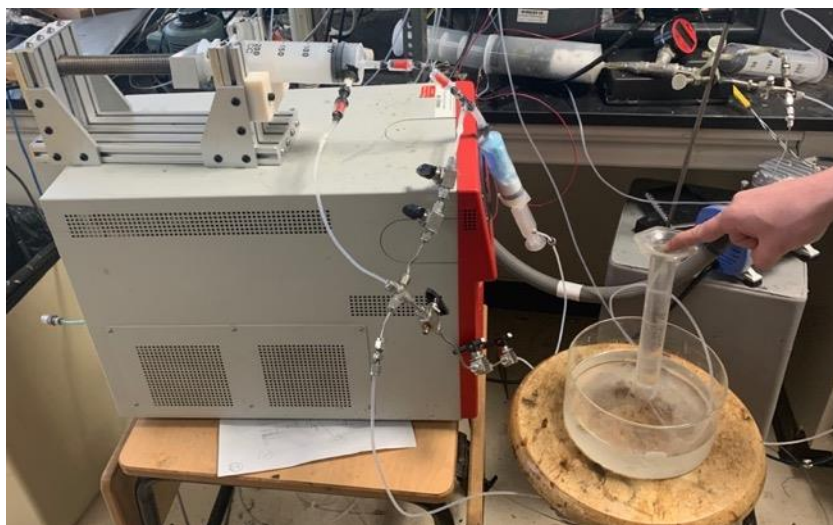


Figure 11: Visual of the volumetric test with the vacuum swing attached.

IR Spectroscopy

The most time-consuming method was the IR spectroscopy method. A vacuum sealed DRIFT cell was utilized in the testing to minimize area detected by the machine and maximize recognition of gases flowing through the system. Calibration of the system was always required whenever transitioning to a new day of data collection. Stage height and windows of the DRIFT cell were manually adjusted to find the best angle of data collection. The spectrum results of the system would then be compared to the base air flow through the system to determine the intensity of gases seen by the system.



Figure 12: Visual of the IR spectroscopy test with the vacuum swing attached.

Results

Due to the immense size of the data tables collected for each compound run through the Analyzer and IR, graphs of the data are shown for their simplification. Complete data sets acquired run into the hundreds of thousands of Excel cells and are omitted to not over-encumber the document. Data sets comparing trends in of base TPSENa is shown across the three systems for comparison averaged after multiple tests.

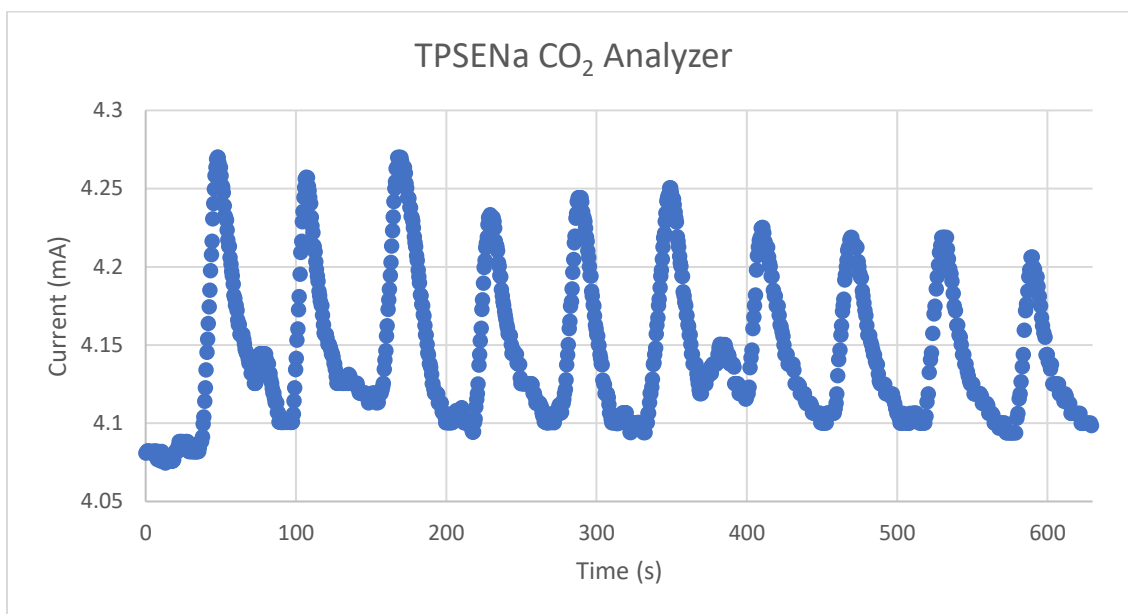


Figure 13: CO₂ obtained after 10 pushes as observed by the CO₂ analyzer for TPSENa.

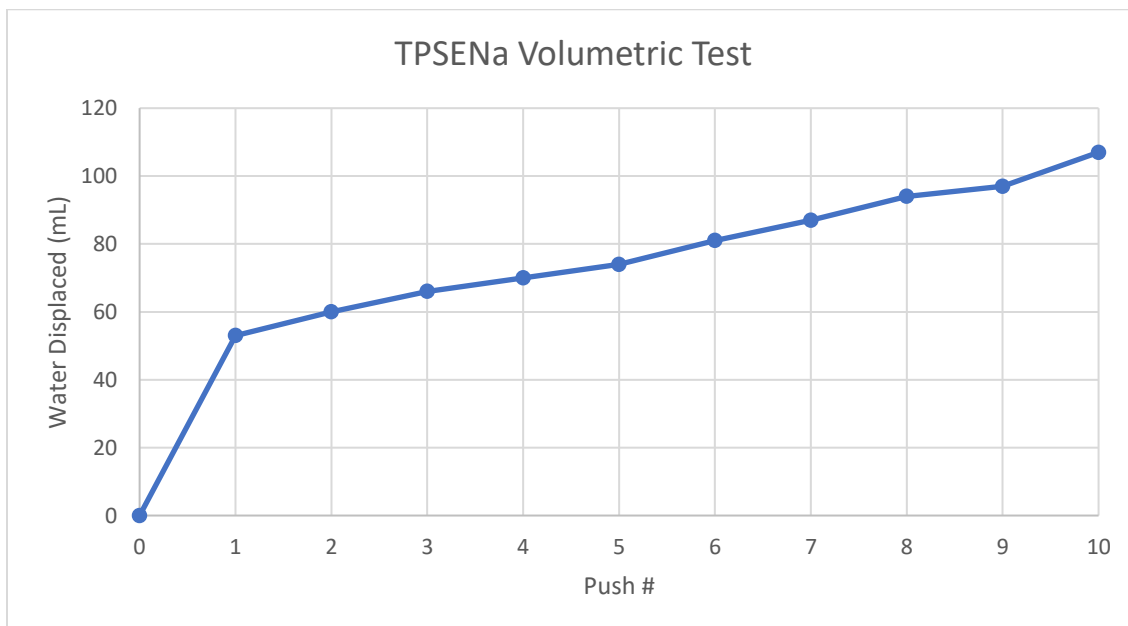


Figure 14: CO₂ obtained after 10 pushes as observed by the Volumetric test for TPSENa.

Peak area analysis

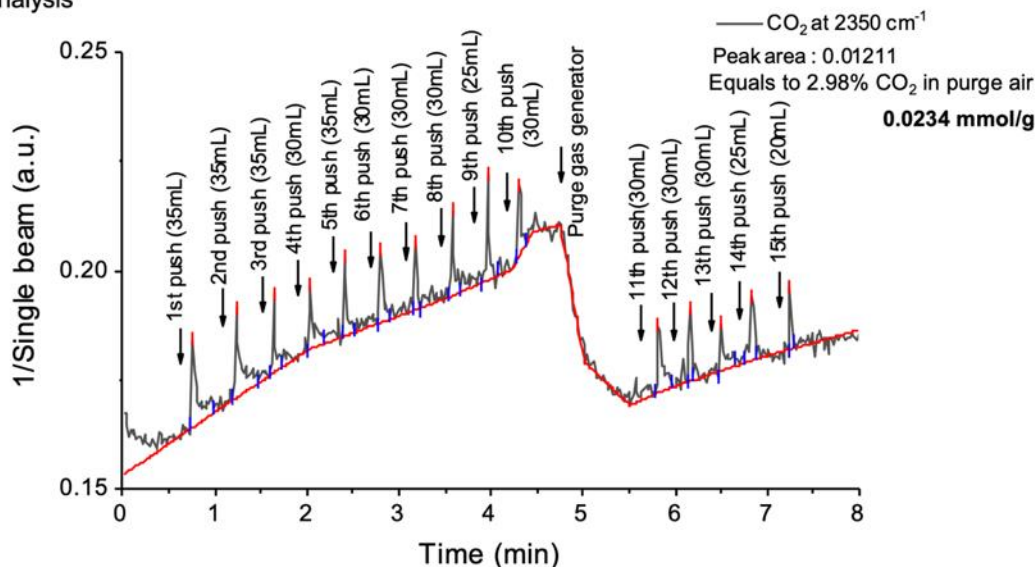


Figure 15: CO₂ obtained after 10 pushes as observed by the DRIFT IR for TPSENa.

The CO₂ analyzer and DRIFT IR indicate component flow by means of peak values, with maximum gases concentrations the peaks when passing through the system. Given the analyzer's propensity to rest at 4.1, the baseline was set in tandem with utilizing integrals of the area below to curve to estimate how much CO₂ passed through the analyzer. The same methodology was applied to the DRIFT IR, though with a shifting curve due to the system being continually jostled when testing. The volumetric test was investigated with the first peak assumed to have 5% CO₂ given the initial push exhaling all system gases, with subsequent pulls assumed pure CO₂ for maximum estimations of system efficacy. Average system total volume outputs were collected and estimated for total CO₂ output. From these methods of analysis, the volumetric test was identified as a helpful secondary test when applied to the analyzer and DRIFT IR for its capacity to determine exact air flow through the system. However, estimates on exact composition through it alone were deemed untrustworthy and not to be run by itself. Between the analyzer and DRIFT IR, the latter was deemed superior due to level of information acquired from the system with the analyzer being somewhat issue prone in events of wire disconnection and pump over encumbrance of the syringe apparatus.

Further testing of various compounds was decided to be conducted with the DRIFT IR to obtain the most complex data sets. Standardized sets of data from the TPSENa, ASPEN, and PU are shown below and their comparison for a best of option.

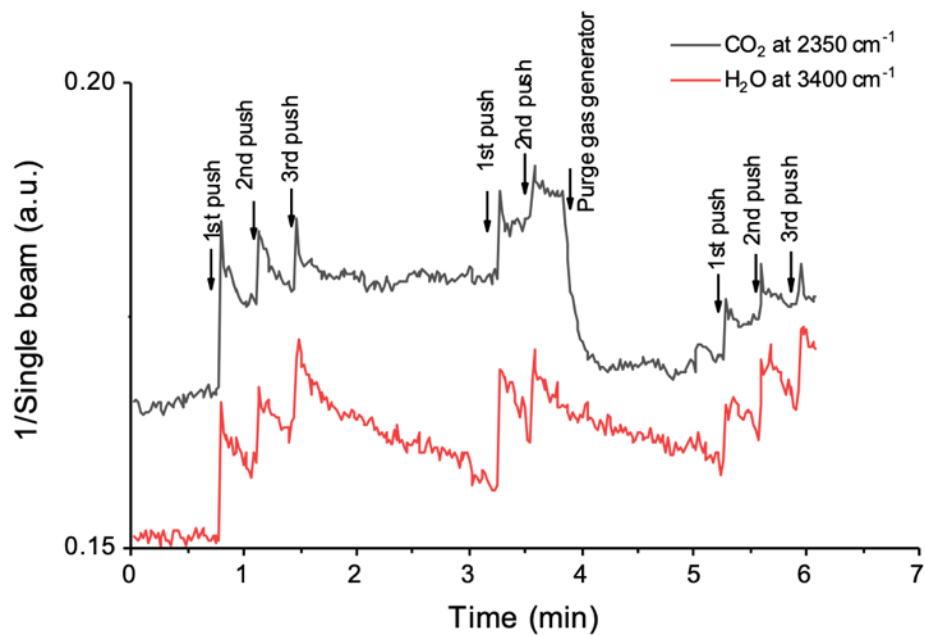


Figure 16: TPSENa data chart obtained from DRIFT IR study.

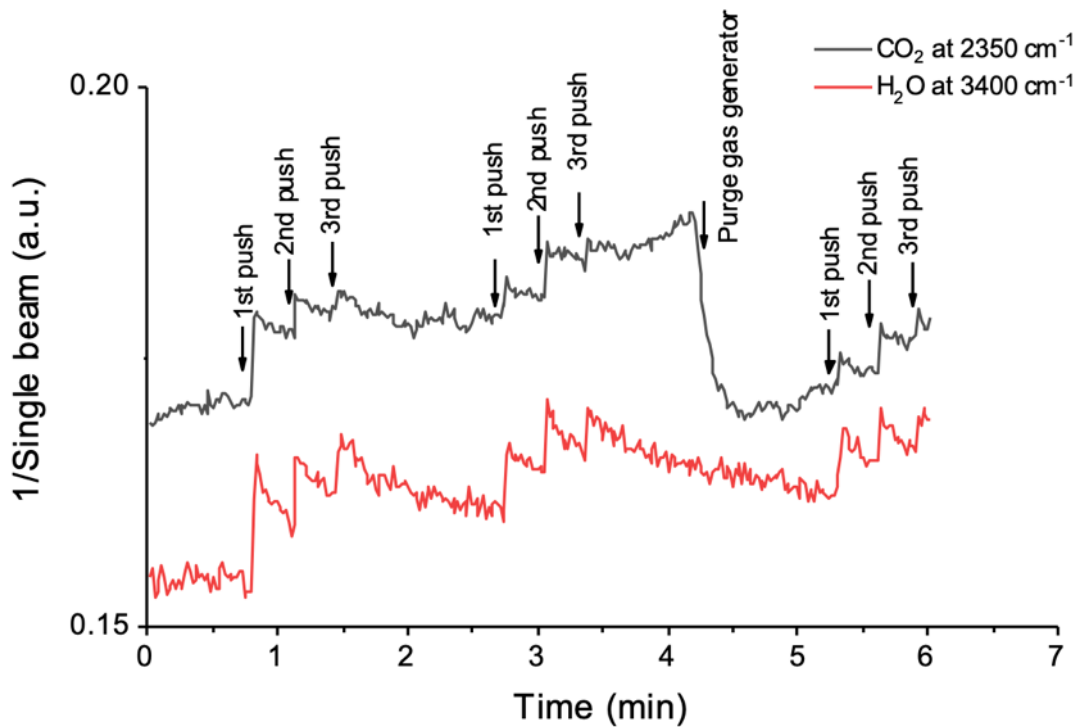


Figure 17: ASPEN data chart obtained from DRIFT IR study.

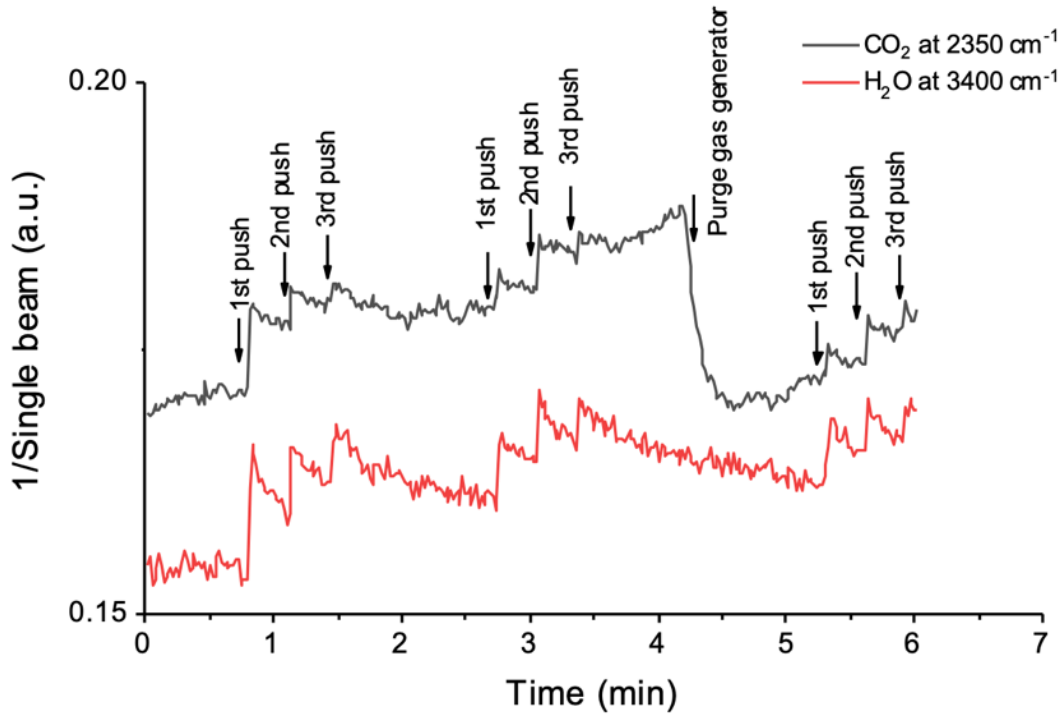


Figure 18: PU data chart obtained from DRIFT IR study.

From the samples tested, areas for multiple three pull cycles were accumulated and averaged over several cycles to account for longevity and reusability. Overall estimates from the tests concluded that the TPSENa data proved the most unanimously superior compound in CO₂ capture capacity reusability, and adaptability for all tested scenarios. Observances of bare DRIFT IR studies display larger and more consistent peaks with TPSENa than those of ASPEN and PU samples.

Discussion

Analysis of the acquired data in tandem with the difficulty of carrying out analysis concludes that using the DRIFT IR is the best method of CO₂ analysis. While the analyzer and volumetric tests excel in simplicity and ease of setup, the capacity to tell how much of what is being observed by the systems is questionable. As stated earlier, the volumetric test is best at determining the total gases contained within the vacuum swing and how much is potential CO₂, but without being in tandem with a separate analyzer is very much a novelty. The analyzer is great at indicating the amount of CO₂ passing through the system, but due to the pumps effect on it and potentially destroying the vacuum seal makes it undesirable. While the DRIFT IR is most definitely the longest setup, once established, it never requires readjustment and can continually pump out data as fast as the user can operate it. While one issue is met with the systems purge gas occurring at undesirable times, it can be looked over due to the wealth of data produced in the end result. It can also be a factor recognized and worked around as done with the data presented, circumnavigating the issue.

Comparison of the sorbents indicates that TPSENa has the highest potential for CO₂ capture and containment. Looking at the DRIFT IR results, PU performs the worst out of the three presented samples, and over variations, even inclusions of the other compounds, still performs worse than pure TPSENa or a majority of ASPEN samples. The ASPEN samples perform notably well, and act as a good baseline of evolution or change for later samples with additions of secondary additives. TPSENa overall performed the best, always beating out other considered compounds regardless of which student made it. Its trends indicate a higher capacity and ability to release over the ASPEN and PU variant. Further additions and adjustments are easily includable to the base substrate for investigation on improvement, further bolstering its potential beyond the data presented.

Conclusions and Recommendations

In summary, the best means of observing and analysing CO₂ capture is through the utility of a DRIFT IR. Faster methods do exist, but the capacity to include what is all vented in addition to knowing CO₂ output is incredibly vital. Moreover, the best amine-based sorbent analysed through this effort was the TPSENa due to both the potential of high capacity and release affinities of its CO₂ capture abilities.

Data from this research indicates further investigation is required in potential faster and equally enlightening methods of analysis, with mass spectroscopy being the foremost advisable method. While this paper has only discussed the general trends of the sorbents researched, more in-depth discussions can be held on the exact qualities and effects of varying sorbent compositions. Lists of effects on both CO₂ and water capture would most certainly be of value on the topic.

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