

# Evaluation of Sorbents for Acetylene Separation in Atmosphere Revitalization Loop Closure

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State-of-the-art carbon dioxide reduction technology uses a Sabatier reactor to recover water from metabolic carbon dioxide. In order to maximize oxygen loop closure, a byproduct of the system, methane, must be reduced to recover hydrogen. NASA is currently exploring a microwave plasma methane pyrolysis system for this purpose. The resulting product stream of this technology includes unreacted methane, product hydrogen, and acetylene. The hydrogen and the small amount of unreacted methane resulting from the pyrolysis process can be returned to the Sabatier reactor thereby substantially improving the overall efficiency of the system. However, the acetylene is a waste product that must be removed from the pyrolysis product. Two materials have been identified as potential sorbents for acetylene removal: zeolite 4A, a commonly available commercial sorbent, and HKUST-1, a newly developed microporous metal. This paper provides an explanation of the rationale behind acetylene removal and the results of separation testing with both materials.

## Nomenclature

|                       |   |                                   |
|-----------------------|---|-----------------------------------|
| <i>CM</i>             | = | Crew Member                       |
| <i>CO<sub>2</sub></i> | = | Carbon Dioxide                    |
| <i>CRA</i>            | = | Carbon Dioxide Reduction Assembly |
| <i>MSFC</i>           | = | Marshall Space Flight Center      |
| <i>OGA</i>            | = | Oxygen Generation Assembly        |
| <i>PCI</i>            | = | Precision Combustion, Inc.        |
| <i>PPA</i>            | = | Plasma Pyrolysis Assembly         |
| <i>QMS</i>            | = | Quadrupole Mass Spectrometer      |
| <i>VVS</i>            | = | Venturi Vacuum System             |
| <i>μGC</i>            | = | Micro-Gas Chromatograph           |

## I. Introduction

THE Carbon Dioxide (CO<sub>2</sub>) Reduction Assembly (CRA) aboard the International Space Station involves the use of a Sabatier reactor to convert metabolic CO<sub>2</sub> to water and methane. The water product is condensed and sent to the Oxygen Generation Assembly (OGA) where it is electrolyzed to provide oxygen to the crew. The secondary OGA product, hydrogen, is then used by the CRA to reduce additional CO<sub>2</sub>. The methane product from the CRA is

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currently vented overboard as a waste product. However, for long-term missions, the hydrogen bound in methane molecules must be recovered to maximize CO<sub>2</sub> reduction in the CRA. For this purpose, NASA is currently exploring the Plasma Pyrolysis Assembly (PPA).

PPA hardware at Marshall Space Flight Center (MSFC) was developed by UMPQUA Research Company<sup>1</sup> and tested at MSFC.<sup>2</sup> During this testing, the PPA was integrated with a CRA development unit and showed promising results. If used in flight, the PPA has the potential to increase oxygen recovery by more than 300 lbm per crew member (CM) per year, beyond CRA alone. This will effectively save approximately 350 lbm of water resupply per CM per year. At a launch cost of \$10,000.00 per lbm, this results in a potential savings of \$14 million per year for a crew of four. However, in order for the PPA to be effectively integrated with a CRA, PPA product hydrogen must be recycled back to the CRA. In addition to product hydrogen and acetylene, the PPA contains un-reacted methane in the product stream. Thus, a separation system must be used downstream of the PPA.

There are numerous methods of separating hydrogen from a gas stream. Among the most mature of these are membrane separations, cryogenic separations, and sorbent-based separations. Membrane separations invariably require a pressure differential across the membrane. Many commercially available units require a differential of at least 2585 torr (50 psid). The PPA operates at 50 torr. To use a membrane separation system, the PPA product gas would need to be pressurized. This is a concern for two reasons. First, acetylene becomes increasingly unstable above atmospheric pressure. Spontaneous decomposition of acetylene, and the subsequent release of energy (explosion), poses a serious safety hazard. Second, pressurizing a gas from 50 torr (~1 psi) to more than 3300 torr (~65 psi) would require a high power compressor as well as accumulators. Thus, membrane separation is not preferred for this application. Cryogenic separations will require a cryogenic source to maintain temperatures. Cryogenic cooling lines are not necessarily going to be readily available on future missions. To make cryogenic cooling available solely for this purpose would prohibitively increase the power requirements of the system. Sorbent-based separations are the most desirable option for multiple reasons. First, NASA has extensive experience using sorbent-based systems, particularly for life support CO<sub>2</sub> removal technology. Second, many sorbents can be regenerated at moderate temperatures or simply vacuum, allowing for low-power systems. Finally, adsorption to sorbents can be completed below atmospheric pressure, providing a system safe enough for acetylene. Thus, for a PPA separation system, sorbent-based separation was chosen for further development.

In previous stand-alone testing, the PPA product stream contained 1-6% methane, 86-89% hydrogen, and 5-8% acetylene (mol %). Due to the hazardous nature of acetylene it is most advantageous to remove acetylene from the PPA product stream. If methane is removed from the product stream, it would be vented as a waste product. This ultimately reduces the recoverable oxygen due to the loss, albeit small, of hydrogen bound in methane. If methane is not removed, it will be recycled to the CRA along with hydrogen. This recycle stream will then contain up to 6% methane. No thorough studies have been completed to determine the effect of methane in the CRA hydrogen feed. It is expected to decrease the total conversion of CO<sub>2</sub> in the system, but further studies will be required to determine the extent of CRA efficiency loss.

Two sorbents have been identified for acetylene adsorption. The first, zeolite 4A, has been shown to readily adsorb acetylene at a wide range of pressures and temperatures (~4.9mmol/g 4A at 273K and 400 torr).<sup>3</sup> Zeolite aggregates were prepared from 4A powder and tested with a variety of gases. Methane showed very low adsorption (0.7mmol/g 4A at 273K and 400 torr). CO<sub>2</sub> was the only gas that showed similar adsorption capacity to acetylene. However, because there is no CO<sub>2</sub> in the PPA outlet stream, 4A shows considerable potential as an acetylene separation sorbent. The second sorbent, HKUST-1, was originally developed in 1999 by Chui, *et al.*<sup>4</sup> Since that time, HKUST-1 has been challenged with a number of different gases. Table 1 provides a summary of these studies and the resulting quantities of adsorbed species. HKUST-1 has also been studied as a possible hydrogen storage medium.<sup>9-10</sup> However, these studies explored hydrogen adsorption at cryogenic temperatures. Hydrogen uptake has been shown to be negligible at ambient temperature and pressure. Thus, based on the low uptake of hydrogen and methane, and

**Table 1. Literature values for uptake of various gases on HKUST-1.** All data were taken at 295K and 1atm with the exception of sulfur dioxide which was taken at 473K at 1atm. All values were approximately determined from literature graphs.

| Challenge Species            | Uptake (mmol/g HKUST-1) |
|------------------------------|-------------------------|
| Propane <sup>5</sup>         | 6.8                     |
| Propylene <sup>5</sup>       | 7.8                     |
| n-Isobutane <sup>5</sup>     | 6.0                     |
| Sulfur Dioxide <sup>6</sup>  | 0.1                     |
| Carbon Dioxide <sup>7</sup>  | 4.2                     |
| Methane <sup>7</sup>         | 0.8                     |
| Nitrogen <sup>7</sup>        | 0.3                     |
| Oxygen <sup>7</sup>          | 0.2                     |
| Nitrous Oxide <sup>7</sup>   | 3.8                     |
| Ethylene <sup>7</sup>        | 5.9                     |
| Ethane <sup>7</sup>          | 4.8                     |
| <b>Acetylene<sup>8</sup></b> | <b>8.7</b>              |

the significant adsorption of acetylene on HKUST-1, the material has significant potential for a PPA separation system.

The purpose of this effort was to explore the use of zeolite 4A and HKUST-1 for acetylene separation from methane and hydrogen as produced by the PPA. This paper details the preparation of sorbent beds, testing methods, testing results, and a discussion of findings.

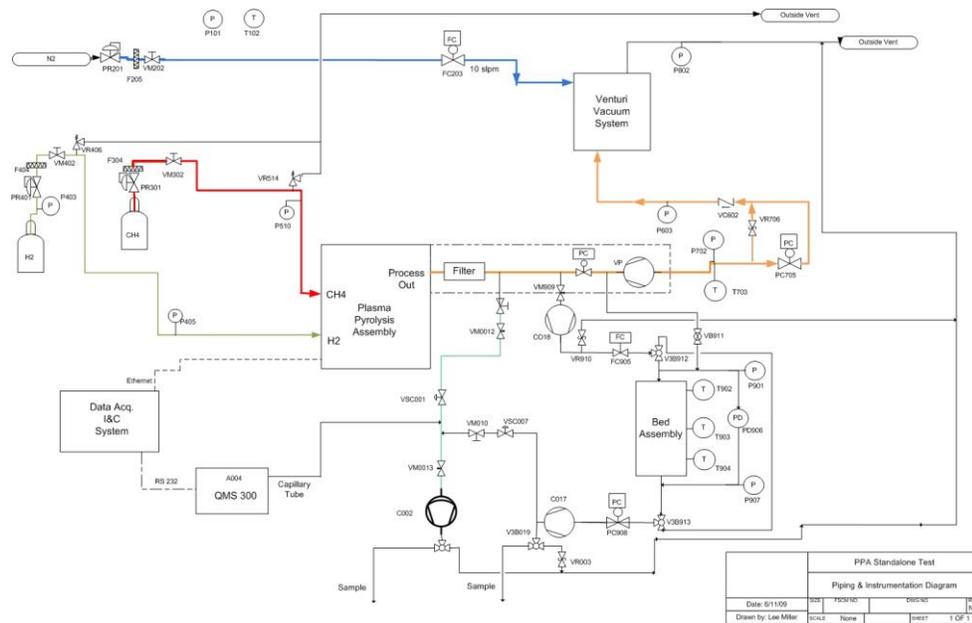
## II. Hardware Description

Hardware used for this testing includes the separation test stand and three separate sorbent beds. Each are described below.

### A. Separation Test Stand

The separation test stand can be seen schematically in Figure 1. The system is composed of the PPA, the sorbent Bed Assembly, a Venturi Vacuum System (VVS), a Data Acquisition system, and two systems for gas analysis including a Stanford Research Systems Quadrupole Mass Spectrometer (QMS), and an Agilent Technologies micro-Gas Chromatograph ( $\mu$ GC). Additionally, the system includes various flowmeters, thermocouples, pressure transducers, etc. for test stand operation.

The PPA, described elsewhere<sup>1-2</sup>, was used in all testing to generate challenge gas streams. Briefly, the PPA,



**Figure 1. Separation test stand schematic. Bed Assembly design allows for interchangeable installation of sorbent beds as required for testing.**

A partial stream of PPA effluent (either ~8% or ~42%) is fed to the Bed Assembly for separation testing. Three-way valves at the inlet and outlet of the Bed Assembly provide a bypass route, if desired. A pressure controller is located between the Bed Assembly outlet and the VVS to control the pressure inside the sorbent bed. When testing, the sorbent bed outlet can either be sent entirely to the VVS, entirely to gas analysis, or be split between the two to allow for both analysis and to control sorbent bed pressure. Each sorbent bed is equipped with its own heating system for regeneration.

The VVS provides a safe avenue for the PPA effluent stream to be exhausted. Methane, hydrogen, and acetylene are diluted with nitrogen in the VVS before being vented outside of the MSFC Test Facility.

The Data Acquisition system is controlled by an in-house program called PACRATS. Data from flow meters, pressure transducers, thermocouples, etc., is collected every second and stored for later analysis.

The test assembly control software is based in LabView and programmed in-house. The software controls all components of the test stand with the exception of the PPA microwave power. This must be controlled by hand.

uses microwave power to generate a hydrogen plasma. Methane is fed to the plasma and partially pyrolyzed to form hydrogen and acetylene gas. The system is maintained at 50 torr by a hydrogen-rated vacuum pump located within the PPA hardware. Hydrogen and methane are supplied to the PPA from locally placed k-bottles.

The flexible design of the Bed Assembly allows for a variety of sorbent beds to be installed.

However, the software monitors the microwave power level and provides warnings if off-nominal conditions are detected.

## B. Sorbent Beds

Two sorbent beds were evaluated for this test. They included a Zeolite 4A Sorbent Bed and a bed containing HKUST-1 Coated Microlith® prepared by Precision Combustion, Inc. Zeolite 4A beads were purchased from Delta Adsorbents (Roselle, IL) and used as delivered. HKUST-1 was purchased from Dr. Banglin Chen's Chemistry group at the University of Texas at San Antonio. Dr. Chen's team was the first to recognize the acetylene adsorption capacity of HKUST-1.<sup>8</sup> Each sorbent bed is described in detail below.

### 1. Zeolite 4A Sorbent Bed

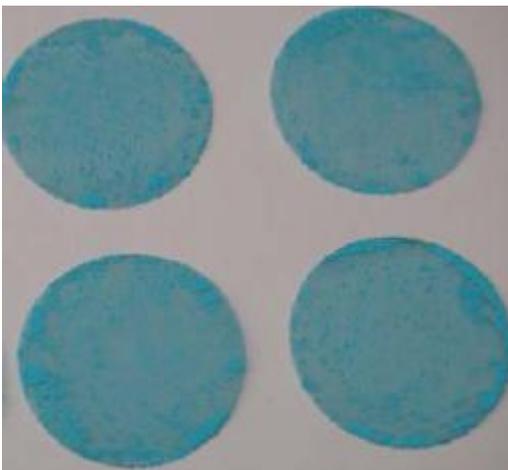
The zeolite 4A bed assembly, shown in , was fabricated from 1.575 cm ID stainless steel tube and packed with commercially procured material in the form of 2.5 mm cylindrical beads. The packed volume has a length of 10.0 cm and contains 32.15 g of 4A sorbent. The assembly incorporates thermocouples to monitor bed temperatures as well as heaters to allow controlled thermal regeneration. The bed assembly is enclosed within an insulated outer shell that allows controlled flow of cooled air over the packed bed assembly. The bed assembly interfaces with the test stand with standard 1/4 inch fittings to simplify installation and configuration.



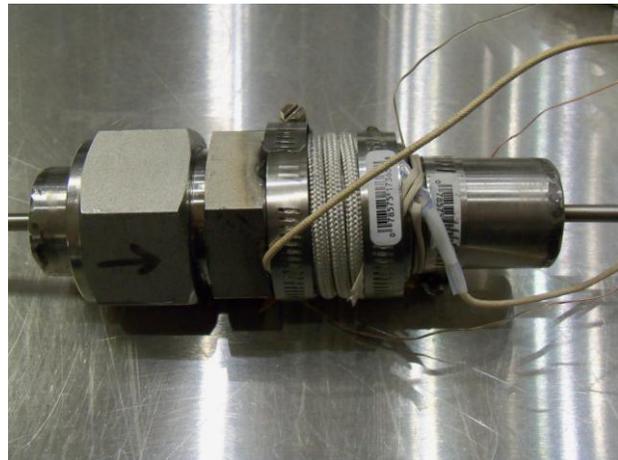
**Figure 2. Zeolite 4A bed assembly.** Assembly contains 32.15 g of 4A sorbent.

### 2. HKUST-1 Coated Microlith®

Due to the powdered form of HKUST-1, immobilization was of key interest for testing. For this purpose, Precision Combustion, Inc. (PCI) was contracted to coat HKUST-1 onto a mesh substrate using their patented Microlith® technology. HKUST-1-coated Microlith® screens can be seen in Figure 3. The sorbent bed housing was fabricated at NASA per requirements provided by PCI. The resulting sorbent bed, shown in Figure 4, has a total volume of approximately 54 mL and contains approximately 6.5 g of HKUST-1. The Microlith® is contained in stainless steel tube measuring approximately 2 inches long with a 1.5 inch inner diameter. The housing tapers to a one-quarter inch tube for installation in the test stand.



**Figure 4. Microlith Screens coated with HKUST-1.** Photo courtesy of Precision Combustion, Inc.



**Figure 3. HKUST-1 Microlith bed assembly.** Assembly contains ~6 g of HKUST-1 sorbent.

### III. Methods

Acetylene separation was explored on two sorbent beds. Each bed was tested at 200, 400 and 600 Torr. Details for the testing of each bed are listed below. The QMS system was operated continuously during all testing to provide composition of the gas stream exiting each bed. Temperature and pressure data were also taken during adsorption. The loading of acetylene onto the bed was calculated for each test run.

#### A. 4A Sorbent Bed

Previous literature indicated substantial adsorption of acetylene in zeolite 4A.<sup>3</sup> For this reason, the first bed tested for acetylene adsorption contained 4A zeolite. The bed was tested in three trials, each with a single repeat, as shown in Table 2. Before each trial, a Full Regeneration at 250°C for 4 hours was performed, followed by cooling to sub-ambient temperature. Each trial included two to three runs in which PPA effluent gasses were fed to the bed at 100 SmLPM or 500 SmLPM until complete breakthrough of acetylene was observed. For each run, a Partial Regeneration was performed after breakthrough by applying vacuum at 125°C for 1 hour.

**Table 2. Testing order and description for 4A zeolite sorption bed.**

| Trial | Pressure | Runs | Partial Regenerations |
|-------|----------|------|-----------------------|
| 1     | 600 Torr | 2    | 1                     |
| 2     | 200 Torr | 3    | 2                     |
| 3     | 600 Torr | 3    | 2                     |
| 4     | 400 Torr | 3    | 2                     |
| 5     | 400 Torr | 2    | 1                     |
| 6     | 200 Torr | 2    | 1                     |

#### B. HKUST-1 Microlith® Sorbent Bed

Xiang *et al.* previously reported extremely high quantities of acetylene adsorption on HKUST-1.<sup>8</sup> For this reason, the second bed tested for acetylene adsorption contained HKUST-1 sorbent obtained from the University of Texas, San Antonio. The bed was tested in three trials, each with a single repeat, as shown in Table 3. Before testing could occur, a one-time initial regeneration was performed at 125°C for 12 hours. Prior to each trial, a Full Regeneration at 125°C for 1 hour was performed, followed by cooling to sub-ambient temperature. Each trial included three runs in which PPA effluent gasses were fed to the bed at 50 SmLPM until complete breakthrough of acetylene was observed. For each run, Partial Regeneration was performed after breakthrough and was conducted by applying vacuum at ~25°C for 1 hour

**Table 3. Testing order and description for HKUST-1 Microlith® sorption bed.**

| Trial | Pressure | Runs | Partial Regenerations |
|-------|----------|------|-----------------------|
| 1     | 200 Torr | 3    | 2                     |
| 2     | 400 Torr | 3    | 2                     |
| 3     | 600 Torr | 3    | 2                     |
| 4     | 600 Torr | 3    | 2                     |
| 5     | 200 Torr | 3    | 2                     |
| 6     | 400 Torr | 3    | 2                     |

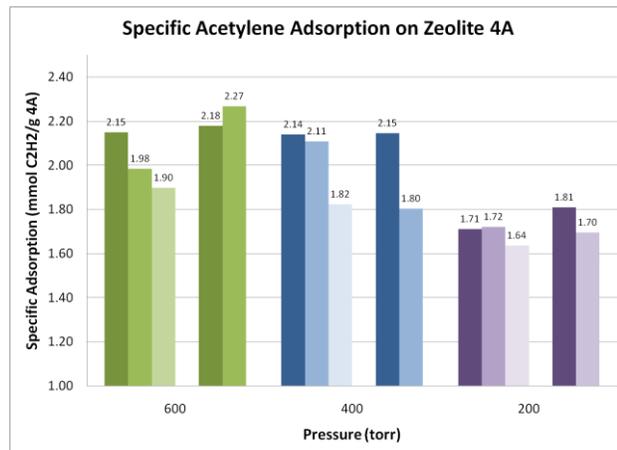
### III. Results and Discussion

Acetylene adsorption was observed on two beds containing either 4A zeolite or HKUST-1. Results of this testing are provided and discussed below.

#### A. Acetylene Adsorption on Zeolite 4A Sorbent Bed

Testing of the 4A sorption bed consisted of three trials with three runs during each trial. Repeats of each trial involved two runs. Partial regeneration was performed between each run and full regeneration was performed between each trial and repeat. Specific adsorption of acetylene for each trial and repeat is shown in Figure 5.

The graph provides a comparison of adsorbed acetylene (mmols) per gram of Zeolite 4A. Data for each trial and its repeat are shown with values listed at the top of each column. For each pressure, trial values are shown first, followed by the repeat. As seen from the data, acetylene adsorption progressively decreases from run to run. This is

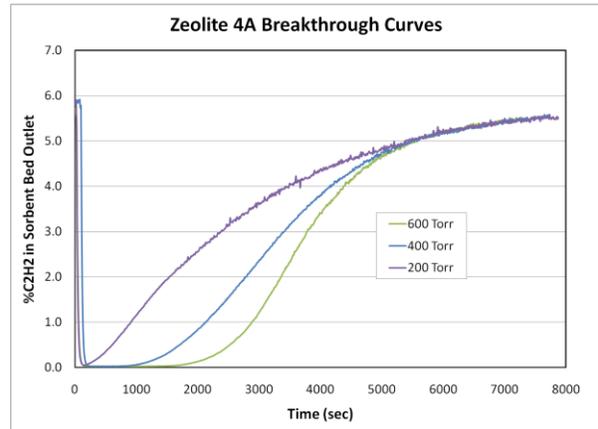


**Figure 5. Specific adsorption of Acetylene on Zeolite 4A at Multiple Pressures.**

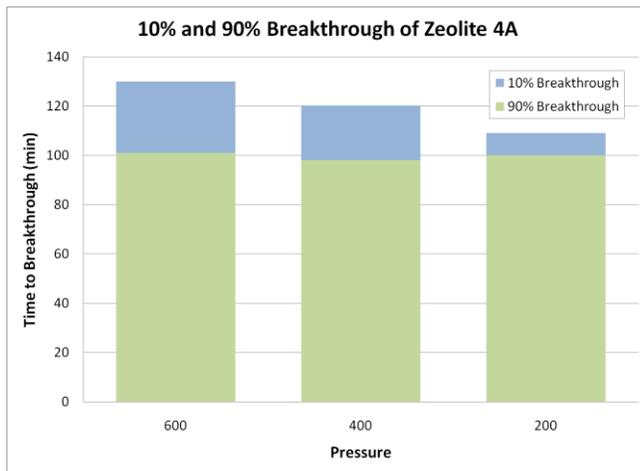
indicative of the Partial Regeneration performed between each run. The Full Regeneration protocol, performed between repeats and separate trials, results in nearly complete regeneration of the sorbent material. In application, it may be possible to use the Partial Regeneration protocol for a given length of time before a Full Regeneration is required. This will allow for smaller sized sorbent beds, reduce power requirements, and possibly reduce the number of beds required for constant acetylene removal. For each pressure, trial and repeats give reasonably consistent values. It is not clear based on temperature, pressure, or operational data why the specific adsorption increased between runs 1 and 2 for the repeat of the 600 torr data point. In fact, the values for each run are close enough that the difference may be statistically insignificant. However, additional testing would be necessary to confirm.

The composition of the sorbent bed exit stream was evaluated (in mole %) using the QMS. Each pressure showed a distinct curve regardless of the amount of acetylene adsorbed. Figure 6 compares exit stream acetylene composition (mol%) during adsorption at each pressure. The adsorption data for each of these curves was taken from the first run of each of the three trials, although each run showed similar curves at a given pressure.

Because it was not always clear where initial breakthrough (point where the bed is no longer adsorbing all of the acetylene in the feed stream) and total breakthrough (point where the bed is no longer adsorbing any of the acetylene in the feed stream) occurred, 10% breakthrough and 90% breakthrough were used to compare adsorption at different pressures. Time was calculated for 10% breakthrough by identifying the point when 10% of the total acetylene feed was passing through the bed. Similarly, 90% breakthrough time was identified by the point when 90% of the total acetylene feed was passing through the bed.



**Figure 6. Mole percent of acetylene in bed exit stream for 600, 400 and 200 Torr.**



**Figure 7. Time to reach 10% and 90% acetylene breakthrough on Zeolite 4A.**

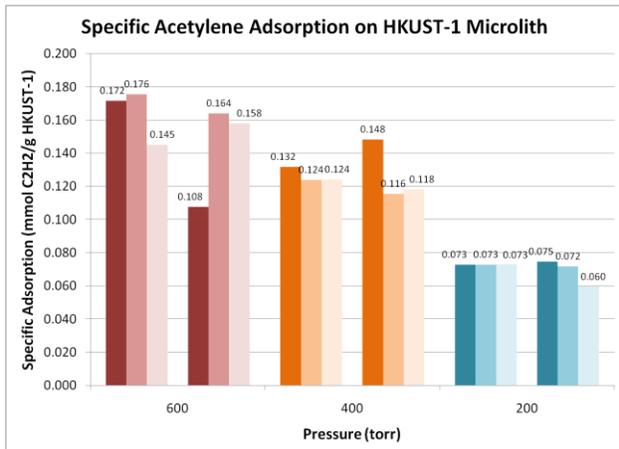
Time to 10% breakthrough was highly dependent on the pressure. Lower pressure resulted in faster 10% breakthrough while higher pressure resulted in slower 10% breakthrough. This can be attributed to the lower capacity of Zeolite 4A for acetylene at lower pressures.

Although the 4A sorbent bed showed significant acetylene adsorption at the conditions tested, initial breakthrough was observed very early in each test. The very gradual breakthrough of acetylene on 4A causes concern for a system in

flight application. Following removal of acetylene, the remaining hydrogen and methane will be recycled to the CRA for additional reaction. There is currently no data for the effect of acetylene on the Sabatier reaction. Before a system containing Zeolite 4A at the given conditions can be used in flight, significantly more testing will be required.

### B. Acetylene Adsorption on HKUST-1 Microlith® Sorbent Bed

Testing of the HKUST-1 Microlith® sorption bed consisted of three trials with one repeat of each trial. Partial regeneration was performed between each run and Full Regeneration between each trial and repeat. Specific adsorption of acetylene for each trial and repeat is shown in Figure 8. The graph provides a comparison of adsorbed acetylene (mmols) per gram of HKUST-1. Data for each trial and its repeat are shown with values listed at the top of

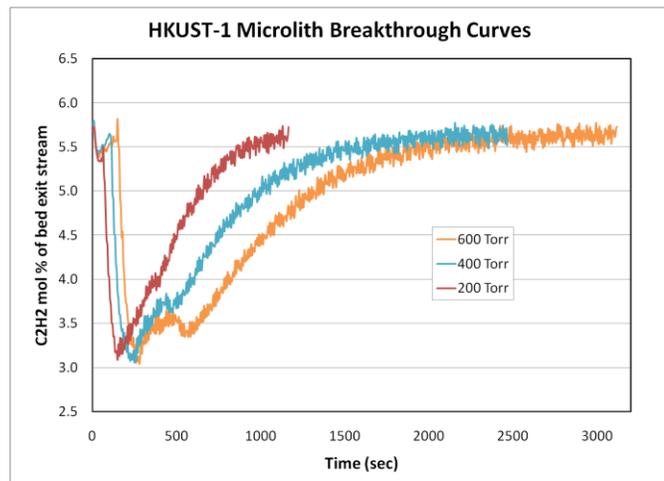


**Figure 9. Specific Acetylene Adsorption on HKUST-1 Microlith® at Multiple Pressures.**

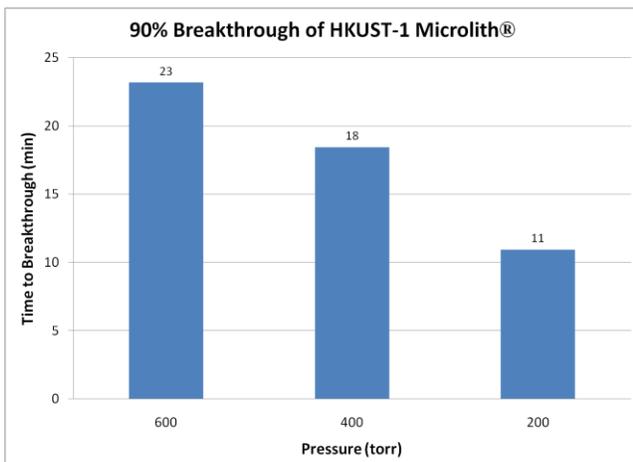
each of the three trials, although each run showed similar curves at a given pressure. As can be seen from the graph, complete acetylene adsorption was never achieved with the HKUST-1 Microlith® bed. Rather, at maximum removal of acetylene, the bed outlet still contained over 3% acetylene at all pressures. This may be explained in three possible ways. First, it is possible that mass transfer was limited through the bed preventing maximum exposure of acetylene to the sorbent material. Second, it is possible that immobilization of HKUST-1 on the Microlith® structure altered the HKUST-1 material, limiting the capacity for acetylene. Finally, it is possible that a significant quantity of the HKUST-1 material was removed from the Microlith due to thermal cycling from initial regeneration. It is clear from this data that testing a bed containing the HKUST-1 powder will be necessary for a

each column. For each pressure, trial values are shown first, followed by the repeat. As seen from the data, there is no apparent trend for adsorption based on runs at 600 torr. Additionally, values for specific adsorption are small enough that the values may not be statistically different. Although variation is observed at 600 torr, values of specific adsorption for 400 torr and 200 torr are very consistent. It is not clear why these differences exist. However, it may be due to differences in flow dynamics at different pressures.

The composition of the sorbent bed exit stream was evaluated (in mole %) using the QMS. Each pressure showed a distinct curve regardless of the amount of acetylene adsorbed. Figure 9 compares exit stream acetylene composition (mol%) during adsorption at each pressure. The adsorption data for each of these curves was taken from the first run of



**Figure 10. Mole percent of acetylene in bed exit stream for 600, 400 and 200 Torr.**



**Figure 8. Time required to reach 90% breakthrough of acetylene on HKUST-1 Microlith®.**

better comparison.

The lengths of the curves shown in Figure 9 are indicative of the quantity of acetylene adsorbed during the test. This is more easily seen graphically, as shown in Figure 10. As described in the previous section, 90% breakthrough is reported because it was not always clear where initial breakthrough (point where the bed is no longer adsorbing all of the acetylene in the feed stream) and total breakthrough (point where the bed is no longer adsorbing any of the acetylene in the feed stream) occurred. HKUST-1 started out at greater than 10% breakthrough, thus this value is not discussed. 90% breakthrough time was identified by the point when 90% of the total acetylene feed was passing through the bed. At higher pressures acetylene took significantly longer to reach 90% breakthrough, while at lower pressures 90% breakthrough occurred much more quickly.

### C. Sorbent Comparison

Based on literature values for adsorption of acetylene on HKUST-1 and Zeolite 4A, neither bed performed as well as anticipated. This can best be seen graphically as shown in Figure 11. While adsorption on the Zeolite 4A was in the general range of the reported values, the HKUST-1 was significantly lower than reported.

During preparation of the HKUST-1 Microlith, it was communicated by Precision Combustion, Inc., that significantly higher loading of the sorbent on the screen was possible. However, development of the bed in this testing was limited by time and resources. Future attempts will likely improve the sorbent loading and possibly improve the overall adsorption capacity. It will also be necessary to test adsorption of acetylene on the powder form of HKUST-1. This will likely result in much higher adsorption. However, in application, a powder-based system is highly undesirable due to pressure drop and possible dusting. Therefore, HKUST-1 immobilization will be imperative if the material is to be used for acetylene separation in conjunction with the PPA and SDU.

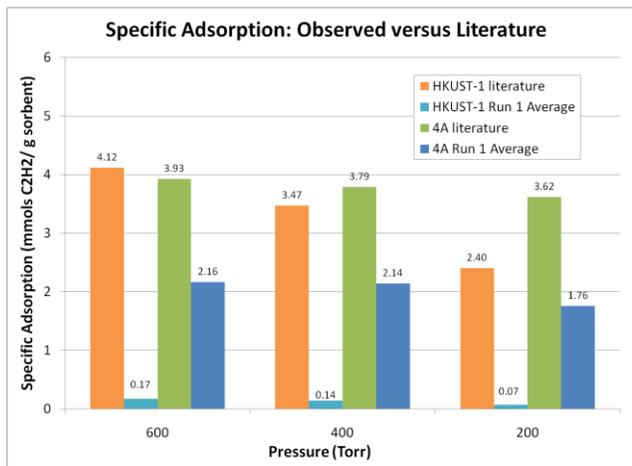


Figure 11. Literature and Empirical Specific Acetylene Adsorption Values for Zeolite 4A and HKUST-1.

## IV. Conclusion

It is clear, based on the data presented here, that significant work is still necessary before an acetylene separation system can be realized for space flight. Neither of the two sorbents tested provided the level of consistent acetylene removal necessary for a flight system. Future work will involve analysis of the effect of a recycle stream from an acetylene separation unit on the performance of a Sabatier reactor as well as additional testing of both sorbents to explore alternative bed designs and/or immobilization techniques.

## Acknowledgments

The authors would like to acknowledge Dr. Banglin Chen at the University of Texas at San Antonio for the synthesis of HKUST-1 and his continued expertise in testing. They would also like to acknowledge Christian Junaedi and Precision Combustion, Inc. for their Microlith® coating efforts. Finally, the authors would like to thank Tom Williams and Kenny Bodkins for their ongoing support with the PPA test stand.

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