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OXYGENATE ONBOARD SEPARATION FOR OCTANE-ON-DEMAND

December 2023

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Abstract

This project further examines the use of Self-Assembled Monolayers on Mesoporous Supports[®] SAMMS[®]-based sorbent materials as a sorbent for alcohols from alcohol-gasoline blends in the context of an onboard separation approach for use in an octane-on-demand strategy. Several questions were posed by potential industry collaborators seeking to better understand how the SAMMS[®]-based materials would perform in a more realistic environment. Several conclusions can be made from the work conducted here, with the caveat that these experiments do not represent the results that would be obtained from continuous or long-term use of the sorbent, because of the short duration of the project. Vigorous extractions into warm gasoline did not reveal the presence of additional species in gas chromatographic analysis. Vibration testing for up to eight hours under aggressive conditions did not show particle attrition. Thermal desorption experiments showed that the SAMMS[®] have a higher capacity for methanol, approximately 50 weight-percent of the sorbent, than for ethanol, approximately 20 weight-percent of the sorbent, and that the methanol is easier to extract. Testing of the A20 fuel blends was insufficient and requires a slightly more sophisticated approach than was attempted here. Additionally, further work would be needed to assess the rate at which the alcohol is absorbed into the sorbent. The testing conducted here suggests that equilibrium is reached in well under an hour. While this study provides additional insights into the use of SAMMS[®]-based sorbent materials for onboard alcohol separation, there is room for further work employing a benchtop testing apparatus similar to that described herein.

Acknowledgments

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Acronyms and Abbreviations

A10	gasoline containing 10% (v/v) methanol
A20	gasoline containing 15% (v/v) methanol and 5% (v/v) ethanol
BOB	blendstock for oxygenate blending
°C	degree Celsius
CARB	California Air Resources Board
E10	gasoline containing 10% (v/v) ethanol
EDA	ethylenediamine
EDA-SAMMS [®]	SAMMS [®] having EDA functional groups bound to the silica surface
EtOH	ethanol
FID	flame-ionization detector
g	gram
G	gravity
GC	gas chromatography
hr	hour
Hz	hertz
lbs	pounds
LDRD	lab-directed research and development
MCM-41	Mobil Composition of Matter No. 41
MeOH	methanol
min	minute
mL	milliliter
μL	microliter
μm	micron
P&ID	pipng and instrumentation diagram
PNNL	Pacific Northwest National Laboratory
SAMMS [®]	Self-Assembled Monolayers on Mesoporous Supports [®]
Si	silicon
Si-DIA	SiliaMetS [®] Diamine
Si-Diol	SiliaBond [®] Diol
Si-DMAP	SiliaBond [®] DMAP (4-Dimethylaminopyridine)
Si-NH ₂	SiliaBond [®] Amine
Si-PHE	SiliaBond [®] Phenyl
SS	stainless steel
% (v/v)	percent by volume

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1.0 Introduction

Engine knock in internal combustion engines, i.e., the auto-ignition of fuel/air mixtures ahead of the primary combustion flame that erodes combustion efficiency, can occur at high engine loads, and is currently a primary factor in engine design and operation. Enabling an octane-on-demand strategy as a means of suppressing knock under high engine loads could increase fuel economy by up to 26% and enable greater design flexibility for engine manufacturers. Onboard ethanol separation allows consumers to use existing ethanolic fuels, likely available for the foreseeable future, and the use of a single pump at a filling station to supply the fuel to the vehicle. The onboard system will separate the high-octane fuel component(s) for use as dictated by the driving conditions. Current approaches, such as membrane separation, have shortcomings that may be overcome using chemical separation approaches recently demonstrated at PNNL using novel solid sorbent materials (Bays, et al., 2021; Grubel, et al., 2019). Further development of these chemical separations approaches may enable a feasible route for adoption and implementation of an octane-on-demand strategy by the automotive industry, adding another option for over-coming current limitations associated with knock.

Solid sorbent materials are likely to provide greater flexibility than current technology (membrane separation), offering the opportunity to more effectively separate ethanol, or oxygenates developed under programs like Co-Optima, without modification of the sorbent material, and have a commercialization track record, as well as at-scale use by the US Navy for submarine air purification. (PNNL, 2012 and Stockton, 2014) Tested oxygenates include ethanol and iso-butanol. However, several questions posed by industry show a gap in knowledge that prevents further development for automotive onboard separation applications. This work attempts to address questions posed by industry.

Previous work (Bays, et al., 2021; Grubel, et al., 2019) identified self-assembled monolayers on mesoporous supports (SAMMS[®]) as a material suitable for separating ethanol from gasoline. SAMMS[®] find their origins in two PNNL patents (Fryxell and Zemanian, 2012; Fryxell, et al., 2009), where chemical functional groups were added in an organized manner to mesoporous silica surfaces. The geometry of the functional groups provided a uniform surface allowing for interaction with materials dissolved in a liquid or a gas.

Questions addressed by this project were expected to generate answers that bridge the gap between laboratory use of SAMMS[®]-based materials and practical application of the materials, with a focus on automotive application. By answering these questions, we have attempted to address a set of barriers identified by industry as hindering further development to guide optimization of SAMMS[®]-based materials for this application. Removing these barriers is essential for the next stage in research/developmental funding, either through the Vehicle Technologies Office or a partnership with industry.

To constrain the scope of work, only SAMMS[®] having ethylenediamine (EDA) moieties attached to the surface, abbreviated as EDA-SAMMS[®], where EDA is ethylenediamine was considered because:

1. SAMMS-chemistry is highly flexible, enabling optimization if required.
2. An analogous material is commercially available (Steward Advanced Materials).
3. The material has been shown to be robust in real world applications by the US Navy. (PNNL, 2012 and Stockton, 2014)

The following represent the areas of investigation that the project sought to undertake. Not all were accomplished in full:

1. Identify/extract trace chemicals from EDA-SAMMS[®] (or DETA-SAMMS[®]) to address concerns about trace impurities contaminating the fuel and entering the combustion chamber.
2. Assess the amount of EDA-SAMMS[®] necessary to separate the ethanol from a tank of gas within 2 hours. Current approach reduces ethanol content from 10% to 2% in 2 hours. (Mizuno, et al., 2018)
3. Partially accomplished: Identify EDA-SAMMS[®] chemical degradation rate and when replacement is needed. This enables economic analysis of separation material and system costs. Mizuno et al. showed a 6.6% loss in membrane performance after 1000 hours of operation. (Mizuno, et al., 2018)
4. Partially accomplished: Assess degradation in a simulated vehicle environment, e.g., attrition rate of the silica substrate as a consequence of vehicle vibration. Effectively no loss in performance for membrane systems after 2M cycles at 6 g and 50 Hz sinusoidal profile was noted. (Mizuno, et al., 2018).

2.0 Experimental Methods

2.1 Chemicals

Gasoline samples were prepared using a California Air Resources Board (CARB) blendstock for oxygenate blending (BOB), received as a sample from a refiner, and used as received. Commercial sorbent materials, SiliaMetS[®] Diamine (Si-DIA), SiliaBond[®] Diol (Si-Diol), SiliaBond[®] Phenyl (Si-PHE), SiliaBond[®] Amine (Si-NH₂), and SiliaBond[®] DMAP (Si-DMAP), were purchased from SiliCycle, Incorporated and used as received. Ethylenediamine-SAMMS[®] was synthesized at PNNL using established methods, using MCM-41 as a substrate. (Zheng, et al., 2005) These materials had particle sizes of approximately 40-63 μm and were used as received. Anhydrous methanol (99.8%) and ethanol (200-proof, $\geq 99.5\%$) were purchased from Millipore Sigma and used as received without further precaution to exclude water.

Sample solutions were made using a volumetric addition approach, where the initial volumes of the components were measured, but not the final volume of the solutions. For example, a 10% ethanol gasoline was blended using 10 mL of anhydrous ethanol and 90 mL of gasoline.

2.2 Gas Chromatographic Analysis of Fuel Samples

Samples were analyzed using an Agilent 6890GC equipped with a flame ionizing detector. The column was an Agilent HP-5MS 30 m x 0.25 mm x 0.25 μm film thickness with a carrier gas of helium at 1.0 mL/min. Oven temperature was initially held for 2 min at 40 $^{\circ}\text{C}$, ramped at 5 $^{\circ}\text{C}/\text{min}$ to 60 $^{\circ}\text{C}$ (no hold), ramped at 25 $^{\circ}\text{C}$ to a final temperature of 200 $^{\circ}\text{C}$. The inlet was heated at 260 $^{\circ}\text{C}$ and 1 μL of sample was injected with a split of 150:1.

2.3 Determination of Contaminants from SAMMS[®] Extractable into Gasoline

Contaminant extraction from sorbent materials was tested by varying time, temperature, and identity of the gasoline-alcohol solution. Sorbent materials analyzed included Davisil, PNNL-made EDA-SAMMS[®] materials, and SiliaMetS[®] Diamine from SiliCycle. One-gram samples of sorbent materials were rinsed three times using gasoline containing no alcohol, then exposed to 5 mL of gasoline containing no alcohol, 10% (v/v) ethanol, 10% (v/v) methanol, and a gasoline containing 5% (v/v) ethanol and 15% (v/v) methanol. Exposures were carried out at room temperature in 20-mL scintillation vials and at 60 $^{\circ}\text{C}$ in 10-mL reactors assembled from Swagelok components. A set of samples was exposed at room temperature for 10 days and a second set exposed for 21 days, after which the liquid was decanted, and each sample was analyzed by gas chromatography (GC), as described in Section 2.2. Heated samples were exposed for 7 days, and the decanted fluid analyzed using the same GC method. Samples were run in triplicate.

2.4 Approximate Determination of Ethanol Uptake Rate

Five 1 gram samples of SiliaMetS[®] Diamine material were dried in a vacuum oven at ~ 100 $^{\circ}\text{C}$ for 1 hour, then soaked in 5 mL of non-ethanolic BOB overnight, after which the residual liquid was decanted from each scintillation vial. Five mL of 10% (v/v) ethanolic gasoline was then introduced and mixed thoroughly with the sorbent material. Following a set time, the liquid was

decanted and analyzed by gas chromatography (GC), as described in Section 2.2. Time intervals tested were 1, 5, 10, 30, and 60 minutes.

2.5 Comparative Assessment for Ethanol Sorption of Functional Groups on Sorbent Materials

One-gram samples of SiliaMetS[®] Diamine (Si-DIA), SiliaBond[®] Diol (Si-Diol), SiliaBond[®] Phenyl (Si-PHE), SiliaBond[®] Amine (Si-NH₂), and SiliaBond[®] DMAP (Si-DMAP) were prepared in scintillation vials and soaked in 5 mL of 10% (v/v) ethanolic gasoline overnight, after which the liquid was decanted from each sample and analyzed by gas chromatography (GC), as described in Section 2.2.

2.6 Determination of Alcohol Capacity and Thermal Desorption of Captured Alcohol

The basic experiment for determining alcohol capacity is outlined in Figure 1. Maximum alcohol capacity of sorbent materials was determined by exposing 3-5 grams of sorbent material to approximately 8 mL of alcohol in a 50 mL round bottom flask, stirring vigorously for 15 minutes removing residual liquid by pipet or syringe, and weighing the sorbent in the flask. The mass uptake of alcohol by the sorbent material represented the greatest capacity of the sorbent for the alcohol. Alcohols tested include neat ethanol, neat methanol, and a three-to-one ratio of methanol to ethanol.

Subsequently, the alcohol was removed via thermal desorption using a short path distillation apparatus while heating the flask in a silicone oil bath and monitoring the temperature of the oil bath by thermocouple. Distillation started at 70 °C for ethanol absorbed in the PNNL-produced EDA-SAMMS[®] sorbent and the SiliCycle SiliaMetS[®] Diamine sorbent, and 65 °C for methanol. The temperature was then ramped slowly to 100 °C and held for one hour, and the mass of alcohol recovered was recorded.

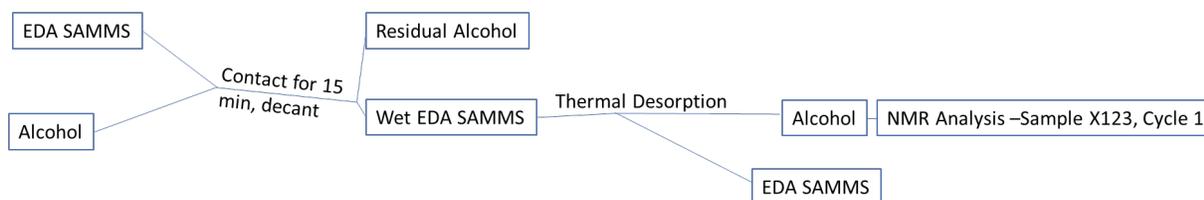


Figure 1. Flow Chart for Determining Maximum Alcohol Capacity of Sorbent Materials. This flow chart shows the basic approach for contacting sorbent samples with alcohol and then thermally desorbing and analyzing the alcohol obtained during the distillation/thermal desorption process.

2.7 Thermal Desorption of Alcohol/Fuel Mixtures from Sorbent Materials

The experiment for recovering alcohols from a fuel mixture is outlined in Figure 2. In these experiments the sorbent materials from the capacity experiments described in Section 2.6 (Cycle 1) were reused. These samples were exposed to 40 mL of alcohol-containing gasoline

by stirring vigorously for 15 minutes at room temperature. The residual liquid was then removed by decanting, followed up by using a pipet or syringe to remove residual liquid. The decanted liquid was analyzed for alcohol content using GC, as described in Section 2.2. The alcohol and trapped fuel were recovered by holding the sorbent at 100 °C for one hour (Cycle 2) using a short-path distillation apparatus. Subsequently, for each additional cycle the sorbent material was exposed to 40 mL of alcohol-containing gasoline at the start of Cycles 3 and 4. During Cycle 3 alcohol was collected at 100 °C for one hour and at 120 °C for one hour, and for Cycle 4 alcohol was collected at 100 °C for one hour, at 120 °C for one hour, and at greater than 120 °C for one hour. The mass of each collected fraction was obtained. When multiple layers were present in the collected fraction, the layers were separated, weighed, and analyzed. Distillate samples containing high concentrations of alcohol were merely weighed, while samples having significant gasoline composition were analyzed quantitatively by GC, as described in Section 2.2, and the alcohol composition determined. Fuels tested included 10% (v/v) ethanol in gasoline (E10), 10% (v/v) methanol in gasoline (A10), and a mixture comprised of 15% (v/v) methanol and 5% (v/v) ethanol in gasoline (A20).

2.8 Vibration Testing of SAMMS[®] Materials

Vibration testing was carried out by Intertek – Plymouth, Michigan. PNNL provided four test samples comprised of granular SAMMS[®] materials enclosed inside of steel tubing, as shown in Figure 3; two tubes contained sorbent test samples saturated with water and two tubes contained only the sorbent samples. All four tubes were then secured to a vibration exciter, 8000-pound shaker from Unholtz-Dickie Corporation, and subjected to a random vibration of 10-1000 Hz at an amplitude of 2 G_{rms} for 4 hours, as noted in Table 1. Test samples were simultaneously subjected to temperature cycling, as noted in Table 2. After four hours Samples 1 and 2 were removed from testing and an additional 4 hours of vibration and temperature testing was performed on Samples 3 and 4. This process was repeated for each of the X, Y, and Z Axes. Samples 1 and 3 were contained only the granular SAMMS[®] material, while Samples 2 and 4 contained the granular SAMMS[®] material immersed in water. Further details can be found in Appendix A in the test report provided by Intertek.

The resulting samples were analyzed on a Microtrac MRB Sync M5000 particle size analyzer using laser diffraction for particle size characterization. Portions from each of the four sample holders were dispersed in a solution of deionized water and Darvan 821A using an ultrasonic cell disrupter at 9 W. Particle size was calculated by adding a subsample to the Microtrac collection reservoir and analyzing it three times.

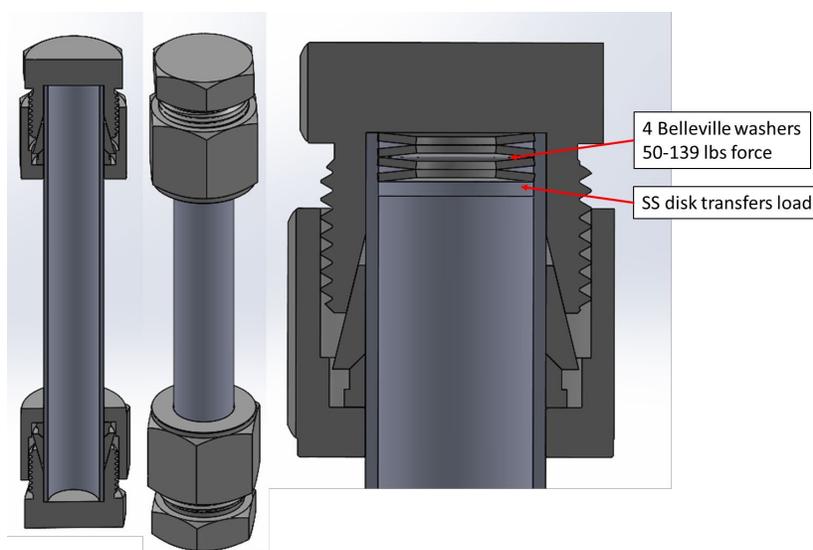


Figure 3. Diagram of Sample Holders for Vibration Testing. The sample holder was designed to be representative of a filter cartridge containing granular filter/sorbent media. From left to right, this figure shows diagrams of a cutaway of the sample holder, an outside view of the sample holder, and a detail of the end fixturing in the sample holder. The end fixturing shows washers used as springs intended to keep the granular material compressed inside the cartridge. The stainless steel (SS) disk was used to transfer the force of the springs to packed filter material. These fixtures were installed on both ends of the sample holder. The sample holder was comprised of a 4 inch section of 0.5 inch outer diameter stainless steel tubing and could hold approximately nine cubic centimeters of sorbent material.

Table 1. Random Vibration Profile for Sprung Masses.

Frequency (Hz)	PSD (G ² /Hz)
10	0.1032
55	0.0336
180	0.0013
300	0.0013
360	0.0007
1000	0.0007

Table 2. Temperature Profile Used for Each Axis.

Time (min)	Temp. (°C)
0	23
30	-40
75	-40
105	23
150	85
205	85
240	23

2.9 System Design for Cycle Testing of SAMMS® Materials

System design for cycle testing was undertaken with the assumptions that the resulting system could:

1. Operate with ethanol, methanol, or a combination of the alcohols in gasoline.
2. Operate as a batch process, rather than a continuous flow process.
3. Use thermal desorption to remove alcohol adsorbed in the sorbent bed.
4. Be scalable, however, the intent was to test up to 100 grams of sorbent material.
5. Be thoroughly instrumented for research purposes.

3.0 Results and Discussion

This section presents the results obtained from several experiments, which, while related in a larger context, are best examined individually.

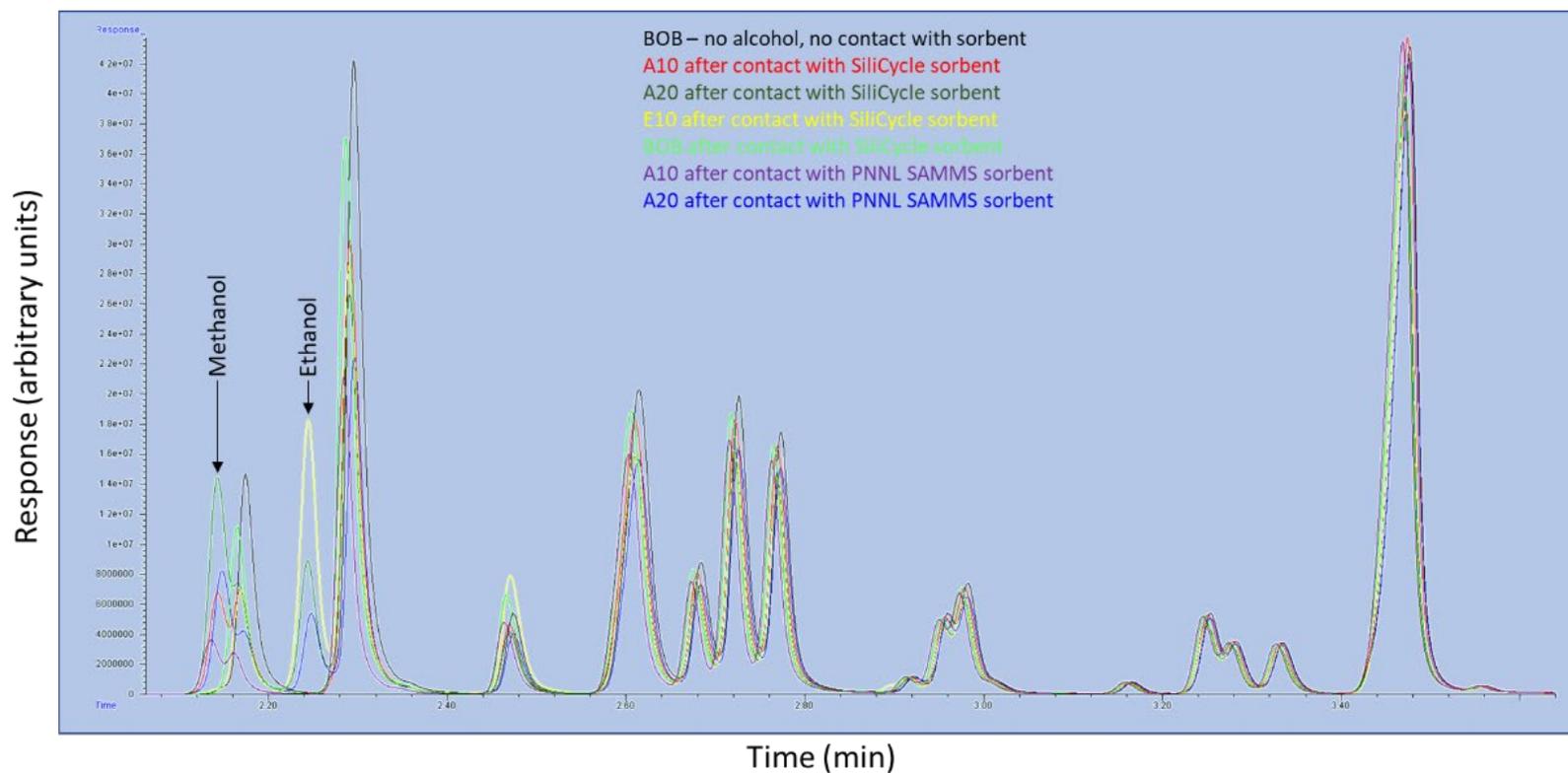
3.1 Evaluation of Impurities from Sorbent Materials

The presence of organic impurities or decomposition products from the sorbent material could have a negative effect upon a vehicle's fuel system or affect combustion. To test whether materials could be washed from the sorbent using gasoline, each sorbent sample was rinsed three times using non-ethanolic gasoline and then allowed to soak in E10, A10, and A20 gasoline at room temperature for three weeks or at 60 °C for one week. The liquid was then decanted and analyzed by GC and the results compared to the gasoline BOB that had not contacted sorbent material. Commercial Si-DIA sorbent and PNNL-produced EDA-SAMMS[®] materials were tested.

Figure 4 shows representative GC chromatograms for fuels having contacted commercial and PNNL-produced sorbent materials at 60 °C. The chromatograms are broken down into three overlapping regions so that the details are more visible. The only differences between the samples exposed to sorbent and the BOB are the alcohols in the fuel samples and small shifts in the retention times. Both are observable in Figure 4a, where the peaks associated with methanol and ethanol are labeled. The slight changes in retention time associated with sample injection account for small misalignments of the peaks in Figure 4a, and are greatly reduced for peaks having longer retention times, like those shown in Figure 4b and Figure 4c. Some changes in peak intensity are also visible, and these are believed to relate to slight differences in sample injection and different relative affinities between the sorbent and a particular fuel component. There are no other obvious changes among the chromatograms, suggesting that any organic materials related to the sorbent that can be washed off or extracted were removed during the sorbent production process. Chromatograms from the room temperature samples were identical to those obtained from the 60 °C samples, although those data are not shown.

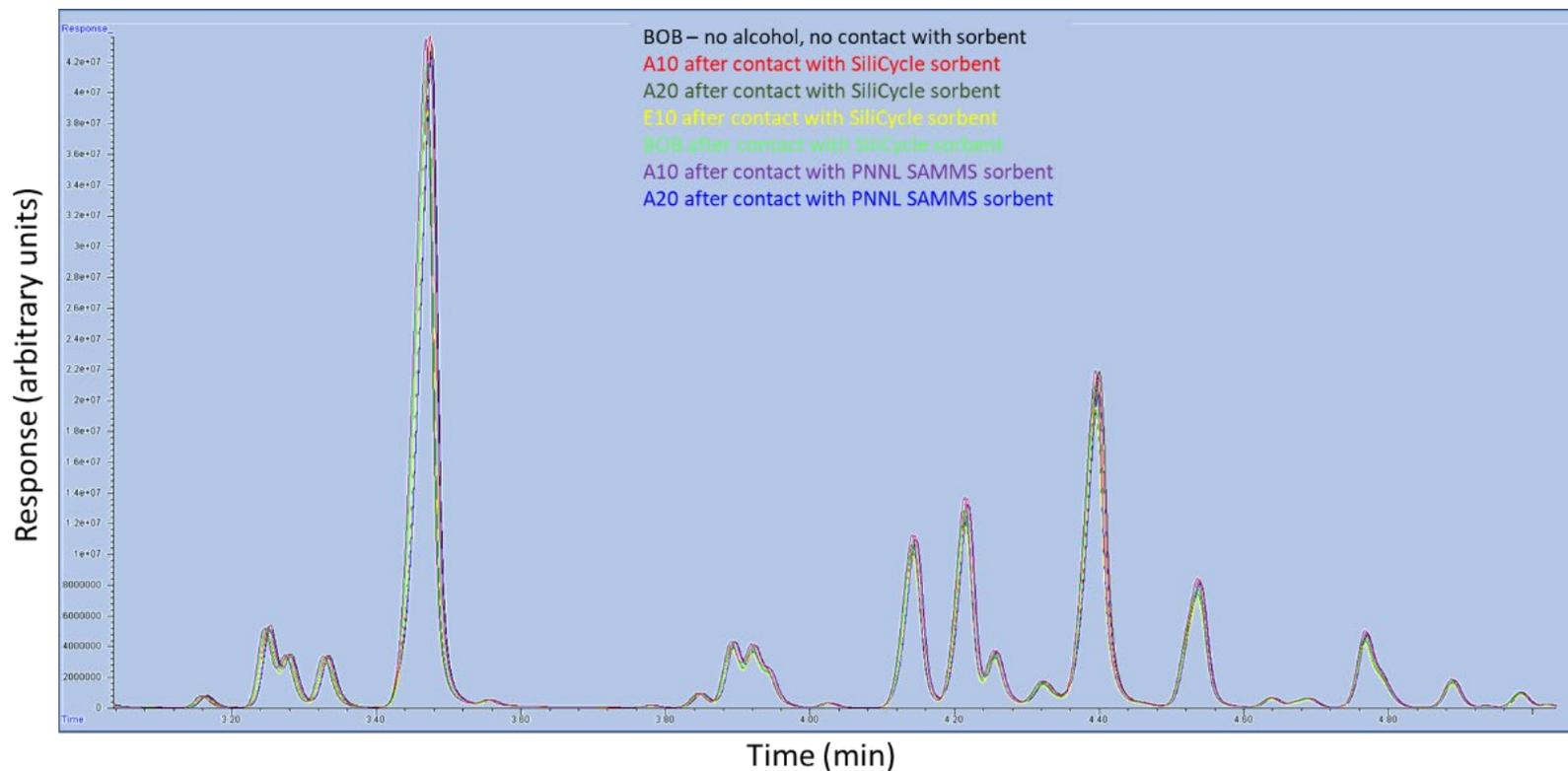
Interestingly, there is also the potential for inorganic contamination from the silica-supported sorbent materials. The slightly acidic nature of methanol and ethanol can promote hydrolysis of silica, particularly when water is present at elevated temperatures. Hydrolysis leads to formation of siloxanes which can be carried away from the sorbent. Decomposition can appear as a change in morphology of the sorbent material, i.e., loss of surface area and pore collapse, or as a milky appearance in the liquid phase. This reaction appears to have occurred, but to an unknown extent, in one of three instances of Si-DIA contacted with A10 fuel at room temperature, but not in the A10 sample held at 60 °C. No decomposition was noted for any other sampling condition, or for the PNNL-produced EDA-SAMMS[®].

The organic monolayer coating is usually sufficient to prevent hydrolysis reactions from occurring under a wide range of conditions, including repeated cycling at relatively high temperatures during distillation. While there is not a good explanation for why this particular sample exhibited hydrolysis, the other samples appeared to remain intact. Additional testing using BET surface area analysis could determine whether slow hydrolysis and pore collapse would occur over time.



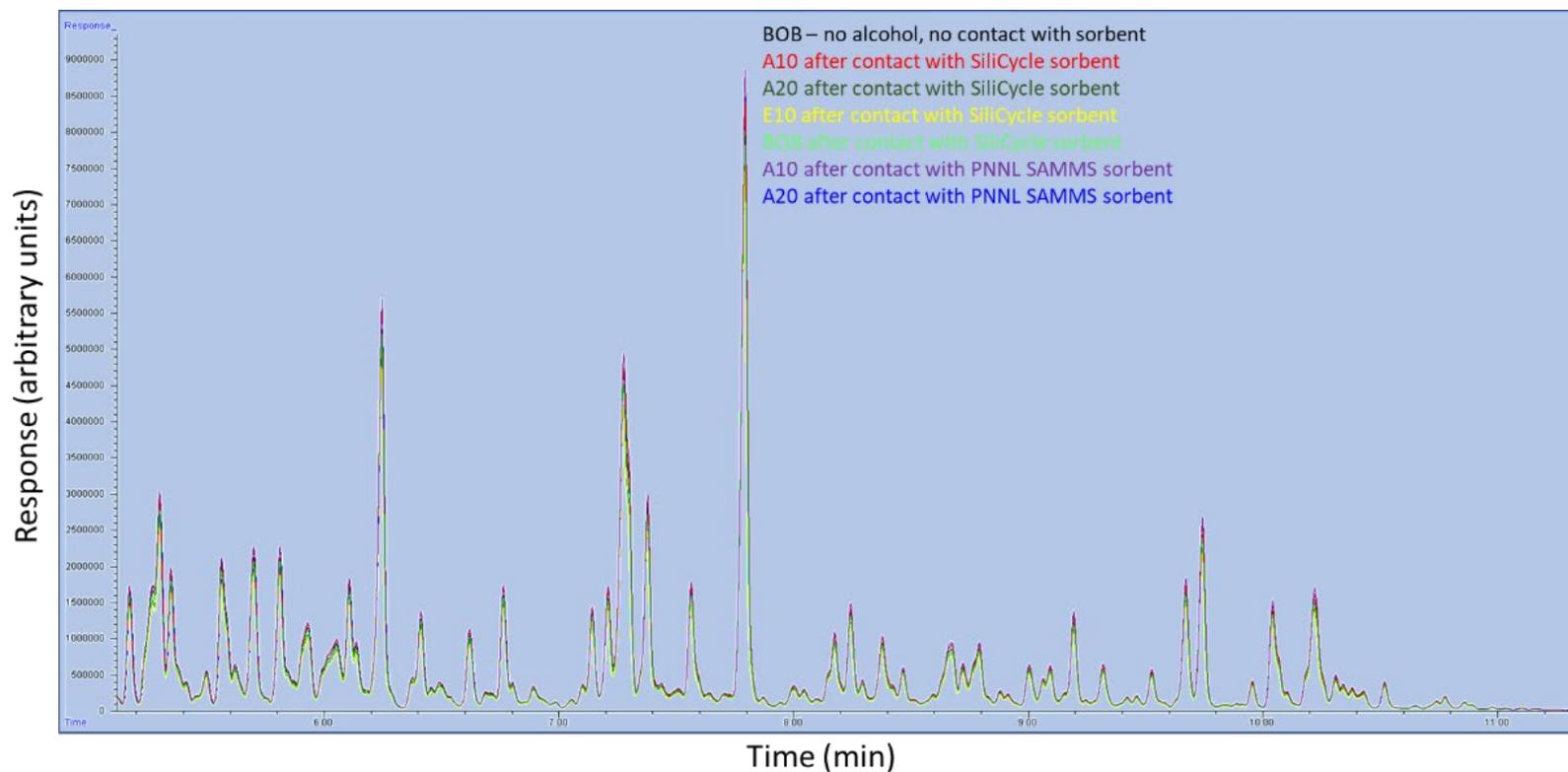
(a)

Figure 4. Overlaid Gas Chromatogram Traces of Neat BOB or Alcohol-containing Fuel Following Exposure of Sorbent Materials. Sorbent materials were exposed to neat BOB or alcohol-containing gasoline at 60 °C for seven days in a pressure vessel. GC chromatograms of the unabsorbed fluid and are shown above, with different retention time windows shown in (a) – (c). Peaks for methanol and ethanol are annotated in (a). Notably, aside from small variations in retention time and alcohol content, no peaks suggesting breakdown of the organic surface were observed.



(b)

Figure 5. (Continued) Overlaid Gas Chromatogram Traces of Neat BOB or Alcohol-containing Fuel Following Exposure of Sorbent Materials. Sorbent materials were exposed to neat BOB or alcohol-containing gasoline at 60 °C for seven days in a pressure vessel. GC chromatograms of the unabsorbed fluid and are shown above, with different retention time windows shown in (a) – (c). Peaks for methanol and ethanol are annotated in (a). Notably, aside from small variations in retention time and alcohol content, no peaks suggesting breakdown of the organic surface were observed.



(c)

Figure 6. (Continued) Overlaid Gas Chromatogram Traces of Neat BOB or Alcohol-containing Fuel Following Exposure of Sorbent Materials. Sorbent materials were exposed to neat BOB or alcohol-containing gasoline at 60 °C for seven days in a pressure vessel. GC chromatograms of the unabsorbed fluid and are shown above, with different retention time windows shown in (a) – (c). Peaks for methanol and ethanol are annotated in (a). Notably, aside from small variations in retention time and alcohol content, no peaks suggesting breakdown of the organic surface were observed.

3.2 Evaluation of Sorbent Functional Groups

In this experiment, similarly-produced mesoporous materials having five different functional groups were purchased from SiliCycle, a commercial vendor. The chemical functional groups tested are shown in Figure 5. In Figure 5 the silica surface is represented by the chemical symbol for silicon, Si, with a circle around it. The topmost chemical structure, Si-DIA (SiliaMetS® Diamine), was the functional group used for all testing outside of this section and can serve as a reference for changes in performance should one of the other materials be used in its place.

With our understanding that the interaction between the sorbent chemical functional groups and alcohols dissolved in gasoline is primarily through hydrogen bonding, the first four materials offer the opportunity to provide a hydrogen-bonding interaction. The fifth material Si-PHE (SiliaBond® Phenyl) does not undergo classical hydrogen bonding but is polarizable and expected to afford some interaction with alcohols through alcohol-induced dipoles.

Figure 6 shows the results of a single competitive sorption study where a gram of sorbent was exposed to 5 mL of E10 gasoline. After exposure, the residual ethanol in the decanted liquid was quantified using GC analysis.

As might be expected, the Si-PHE was the poorest-performing material because the pores in the sorbent are coated with non-polar phenyl rings, which do not form hydrogen bonds with the ethanol. For the other chemical functional groups tested, the Si-Diol provided the greatest ethanol uptake, while the single-amine moiety, Si-NH₂, had the lowest uptake. Because of the greater polarity associated with the diol moiety, it is not surprising that Si-Diol should perform better than either of the primary and secondary amine-containing materials, however, the intermediate performance of the Si-DMAP is not as readily explained by the perspective of hydrogen bond polarity, because of the lack of protons capable of forming a hydrogen bond. While there are no hydrogen atoms available for hydrogen bonding, the tertiary amine site can be a hydrogen bond acceptor, as can the aromatic pyridinyl nitrogen. The polarized nature of the pyridinyl ring may also be beneficial from the perspective of forming a polar environment for the ethanol. Additional testing may provide useful insights into the performance of these and other materials.

While these results suggest an order of preference for ethanol, the span amongst these four materials is only seven percent, and are derived from a single set of experiments, so too much should not be read into these results without a more definitive study. These results suggest that materials that have stronger hydrogen bonding functional groups will have a greater affinity for alcohols in gasoline. These materials should not be judged solely on higher affinity, because higher affinity may also contribute to higher desorption temperatures. A balance must be struck, suggesting further testing would be needed to fully assess these materials in an onboard separation application.

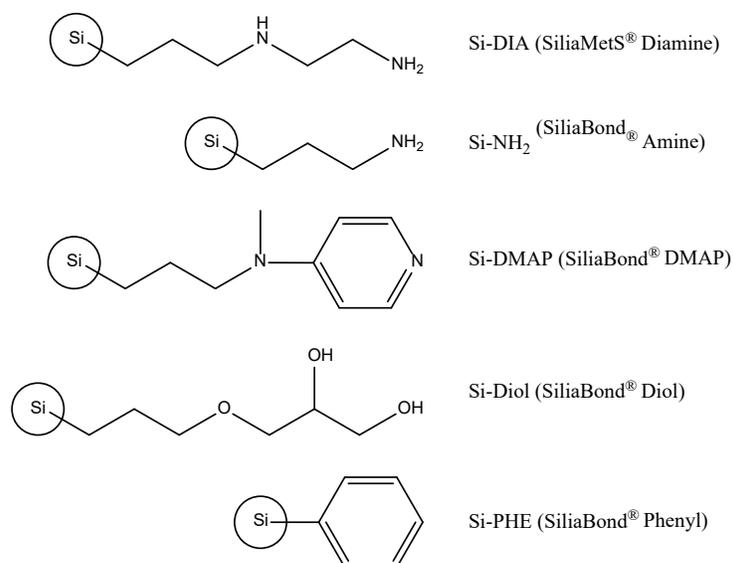


Figure 7. Chemical Structures of Sorbent Functional Groups. Sorbent materials are porous silica structures that are lined with chemical functional groups. This figure shows the chemical functional groups tested for the comparative ethanal sorption tests described in Section 2.5. In this figure, the circle with Si in the center is intended to represent the silica substrate. Most of the testing in this study was carried out using the Si-DIA sorbent from SiliCycle. Some testing was carried out using EDA-SAMMS[®] material, having self-assembled monolayers with the same chemical functionality as shown for the Si-DIA sorbent.

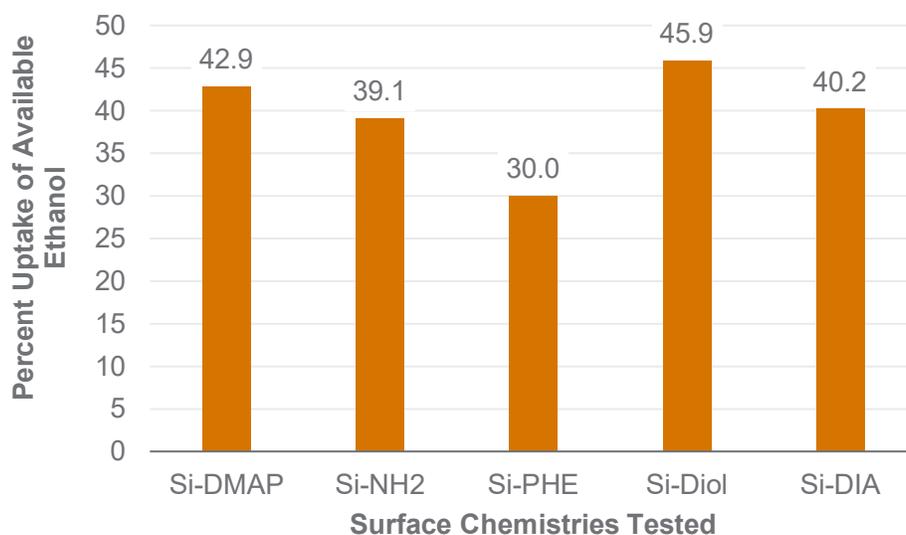


Figure 8. Comparative Test of Ethanol Uptake by Commercial Sorbents. This chart shows the percentage of available ethanol absorbed by the indicated commercial sorbent material from a 10% (v/v) ethanolic gasoline, as described in Section 2.5.

3.3 Absorption Rate Experiment

SAMMS[®]-based sorbents are known for high surface areas and open pore architectures. (Zheng et al. 2005) The same is true for the sorbent materials purchased from SiliCycle, where the surface area is advertised to be between 480 and 550 m²/g and the pore size is between 55 and 65 Å. (SiliCycle 2022) The open architecture facilitates mass transport into and out of the sorbent pores, allowing for rapid interactions with moieties bound inside the pores. (Fryxell et al. 2004; Bitterwolf et al. 2004)

In this experiment, a gram of Si-DIA sorbent, having been soaked in BOB overnight, was contacted with E10 gasoline and a sample of the liquid removed and analyzed by GC after the specified contact time for the residual (unabsorbed) ethanol. Unfortunately, the GC measurements of ethanol were not performed quantitatively, and so are presented normalized to a peak from the gasoline BOB. This allows for a relative comparison of the ethanol present, as compared to a specific chemical in the gasoline. While not ideal, under the assumption that the gasoline component has little or no affinity for the polar Si-DIA sorbent, this approach provides a means of comparing the ethanol content between samples. This was tested by comparing the ratios of a different chemical in the gasoline and the ethanol, and a comparable trend was observed. Another unfortunate aspect of this experiment is that a GC of the E10 fuel was not obtained, so there is no reference value for a ratio of the ethanol peak and that of the gasoline component from which to compare.

Time-dependent data are shown in Figure 7. Notably, each sample was prepared separately, so an individual sample was not tracked over time. This inherently introduces some variability among the samples.

Observations that can be made from the plot in Figure 7 suggest that there is very little change in the relative ethanol concentration over the course of an hour. There may be a slight trend downward over that hour. There is some data scatter among the samples representing the first ten minutes of E10 contact with the sorbent.

While these observations do not lead to a definitive conclusion, they are consistent with an ethanol concentration stabilizing shortly after the E10 gasoline contacted the sorbent, which is consistent with observations made by Fryxell and coworkers that equilibrium was established within one minute for a lanthanide species absorbed by a comparable SAMMS[®] sorbent. (Fryxell et al. 2004)

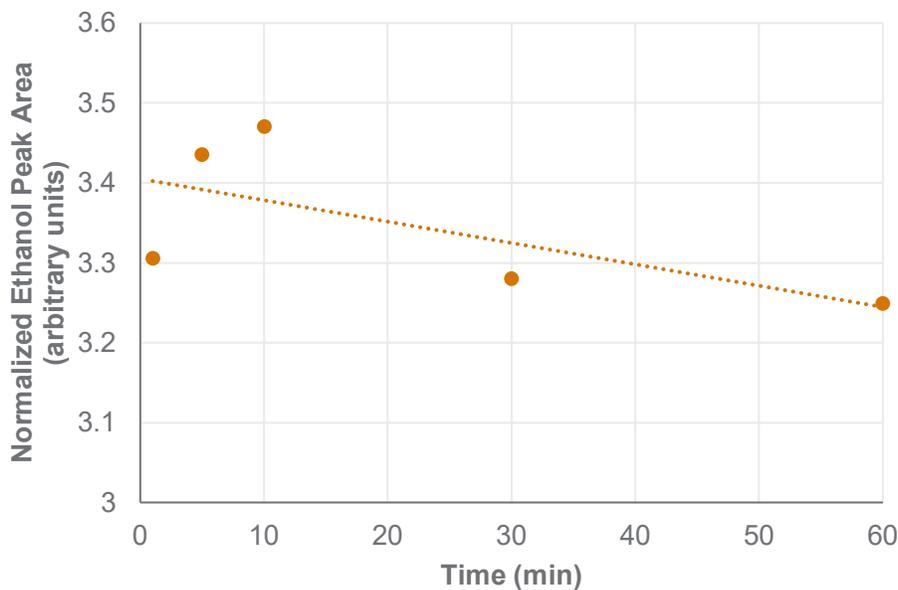


Figure 9. Test of Ethanol Uptake Rate. This chart shows that the relative amount of ethanol remains unchanged over the course of an hour following addition of 1 gram of Si-DIA sorbent to 5 mL of 10% (v/v) ethanolic gasoline. The data was obtained qualitatively. In order to allow comparison of the peak areas between samples, the area of the ethanol peak was divided by the area of an arbitrary peak from the gasoline BOB. The differences between samples are small, suggesting that ethanol absorption into the sorbent is fast.

3.4 Absorption-Thermal Desorption Experiments

This set of experiments was intended to show the flexibility of the sorbent material for partitioning alcohols from an alcohol-gasoline blend and the ability to recover the alcohol using thermal desorption. Three alcohol-gasoline blends were examined: a 10% (v/v) ethanol-gasoline blend (E10), a 10% (v/v) methanol-gasoline blend (A10), and a blend of 15% (v/v) methanol, 5% (v/v) ethanol and gasoline (A20).

Two types of experiments were performed to gain an understanding of the sorbent material for each alcohol/alcohol-gasoline blend in gasoline. In the first set of experiments, the Si-DIA sorbent was exposed to a neat alcohol or alcohol blend, the liquid decanted, and then the distillate collected at three different temperatures. Except as noted each distillate cut was examined by GC. These experiments are described in Section 2.6 and shown graphically in Figure 1. Results are shown in Table 3 and will be discussed subsequently. In the second set of experiments, each batch of Si-DIA sorbent was exposed to the respective alcohol or alcohol-gasoline blend, the free-flowing liquid was then decanted, and the liquid captured in the sorbent was thermally desorbed. During an experiment, the sorbent was exposed once to the pure alcohol/alcohol blend, and three times subsequently to the alcohol-gasoline blend. Following exposure to the alcohol-gasoline blends, increasingly higher temperatures were used to recover the absorbed liquids. In most cases the distillate was examined by GC to observe its composition. This process is more thoroughly described in Section 2.7 and Figure 2. Results are shown in Table 4, Table 5, and Table 6, and discussed subsequently. Notably, the experiments were designed such that the capacity of the sorbent material was smaller than the amount of

alcohol in each alcohol-gasoline sample, such that an equilibrium could be reached without greatly depleting the alcohol in the free-flowing liquid.

Understanding the amount of alcohol and fuel recovered in Tables 3 – 6 was not straight forward. Measurement challenges were observed for the gravimetric analyses, which account for liquid retained in the sorbent and between the sorbent granules, and for the GC analysis, which measured the loss of alcohol from the decanted liquid. These challenges contributed to uncertainties which were carried into subsequent experiments. Additionally, some of the distillate cuts were biphasic, requiring the phases be separated and considered individually. All of the distillate cuts were not analyzed by GC, as noted with an asterisk in each table, and are likely some combination of alcohol and gasoline. These gaps in analysis resulted in values recorded for alcohol recovered that are higher than expected and percent recovered values often exceeding 100 percent. However, the trends are important to observe and reflect the affinity of the sorbent material for specific alcohols.

Continuous Thermal Desorption Experiments

Table 3 presents the results of the SiliaMetS[®] Diamine (Si-DIA) sorbent material exposed to A10, A20, and E10 fuels. In these experiments the mass of alcohol retained was obtained by measuring the mass of the fluid decanted after contacting the sorbent. The mass retained reflects the mass of fuel (alcohol and gasoline) contained in the wet sorbent material and in the interstices between the particles. Significantly, based upon the gravimetric and GC analyses, a considerable amount of alcohol was absorbed into the sorbent material, ranging from ~45% of the available methanol in the A10 fuel to slightly more than 20% of the alcohol available in the A20 and E10 fuels. This equates to 0.47 grams methanol per gram of sorbent from the A10 fuel and 0.22 grams of ethanol per gram of sorbent from the E10 fuel.

Interestingly, while the grams alcohol recovered and percent recovered slightly exceeded the grams alcohol retained in the A10 experiment, the methanol was able to be recovered effectively quantitatively, as was the base fuel. The methanol and fuel eluted as a single fraction with no obvious phase separation. Sample handling and fuel volatility were likely contributors to the apparent excess in alcohol recovered from the sorbent.

Recovering ethanol from the E10 experiment was not as easy as methanol in the A10 experiment. Only 22 percent of the trapped ethanol was recovered for distillation ranges up to 150 °C, and this was likely carried over with the base fuel. Higher distillation temperatures were not attempted in this set of experiments. The distillates for each temperature range were homogeneous. GC analysis of each fraction showed that mostly base fuel was recovered at these temperatures.

The A20 experiment was more challenging to understand since the alcohols were not clearly differentiated in the analyses. The 100 °C distillate was comprised of two layers with the top layer consisting primarily of fuel, while the bottom layer was comprised primarily of alcohol, but not analyzed by GC. Distillates recovered at the two higher temperatures were not further analyzed. GC analysis of the <100 °C layer showed that the layer was comprised primarily of distillate from the base fuel with only a very small amount of ethanol and methanol recovered. Considering the results from the E10 experiment, it is likely that only small amounts of ethanol were recovered in each distillation cut and most of the ethanol remained in the sorbent. Similarly, from the results of the A10 experiment, most of the methanol was likely recovered in the fraction desorbed at <100 °C with very little distilling at higher temperatures. This understanding might be used to provide a better indication of the Total Alcohol Recovered value

that is noted in Table 3, 1.18 grams of alcohol and 153 percent recovered, which suggests that the collected fractions contain significant contributions from the base fuel. Making some assumptions that 0.60 grams of base fuel-alcohol mixture is roughly 75 percent alcohol, based on the A10 experiment, and the values for the E10 experiment are substituted for the temperature ranges of 100-120 °C and 120-150 °C, the percent alcohol recovered becomes much more reasonable at about 84 percent. While there is significant room for error because of how this figure was derived, it is likely that nearly all of the methanol and some of the ethanol can be recovered from A20 at temperatures <150 °C.

The continuous thermal desorption experiments suggest that recovery of methanol, whether from A10 or A20 fuel blends, occurs readily at <100 °C, and is nearly quantitative, and that higher temperatures are necessary to recover ethanol.

Repeated Thermal Desorption of 10% Methanol-Containing Fuel (A10) from Sorbent Materials

Table 4 shows the results from a series of thermal desorption steps after contacting Si-DIA with neat methanol and then A10 fuel. The results presented are relatively straight forward. Following contact of the sorbent with neat methanol, 82 percent of the methanol was recovered at <100 °C. Similarly, after the first contact with A10 fuel, 73 percent of the methanol was recovered in Cycle 2. Subsequent thermal desorptions produced yields >100 percent when all of the fractions were considered. This suggests that the fractions captured at >100 °C are comprised largely of base fuel components. Removing these values provides alcohol recovered yields of nearly 113 and 73 percent, respectively. The high yield associated with Cycle 3 may result from buildup of methanol in the sorbent over Cycles 1 and 2, followed by increased yield at <100 °C during Cycle 3. The Cycle 4 yield is in keeping with that observed for Cycle 2.

Repeated Thermal Desorption of 10% Ethanol-Containing Fuel (E10) from Sorbent Materials

Table 5 shows results for a fresh sample of Si-DIA sorbent contacted with neat ethanol, followed by three cycles of E10 fuel. Similar to the results presented for the A10 experiment, yields after the first Cycle exceed 100 percent. For Cycle 2, where desorption is <100 °C, the yield exceeds the alcohol taken up by the sorbent material. This can be explained by ethanol not thermally desorbed during Cycle 1 contributing to the increased yield in Cycle 2. The higher boiling point of ethanol likely contributes to this being observed in Cycle 2, as opposed to Cycle 3, as observed for the A10 experiment. Subsequent cycles, show yields that exceed 100 percent. If the data are treated by ignoring contributions from fractions above 100 °C, the yields are closer to those observed for E10 during the continuous thermal desorption experiments at nearly 20 percent for Cycle 3 and considerably higher for Cycle 4 at nearly 50 percent.

Repeated Thermal Desorption of 15% Methanol/5% Ethanol-Containing Fuel (A20) from Sorbent Materials

Results for the A20 experiment are shown in Table 6. As for the continuous thermal desorption experiments, having two alcohols complicated the analysis of the A20 fuel results by causing phase separation for the first distillate cut. In these cases, the layer rich in base fuel was analyzed via GC, while the alcohol-rich layer was not further analyzed.

The Cycle 1 exposure of the Si-DIA sorbent to neat alcohol (75% methanol/25% ethanol by volume) returned most of the alcohol, which presumably had only a small ethanol component because of the low thermal desorption temperature. The Cycle 2 yield exceeding 100 percent might be expected because of the desorption of alcohol not recovered during Cycle 1, however,

this value is less clear because of the “alcohol” layer, which was not analyzed by GC and likely contained some base fuel, artificially increased the yield. Discounting fractions desorbed at >100 °C, as described previously, adjusts the yield for Cycle 3 to approximately 80 percent, and the yield for Cycle 4 to approximately 89 percent. These should also be adjusted slightly lower to account for the base fuel in the alcohol layer desorbed at <100 °C.

Key Observations

- Methanol can be absorbed from an A10 fuel at roughly 50 weight percent of the sorbent.
- Methanol is readily recovered from the sorbent at temperatures <100 °C.
- Ethanol can be absorbed from an E10 fuel at roughly 20 weight percent of the sorbent.
- Higher temperatures are required to recover ethanol from Si-DIA sorbent than were applied during this series of experiments. Alternately, addition of a vacuum could be helpful.
- Gasoline will be a portion of every fraction captured and desorbed.

Table 3. Single, Continuous Thermal Desorption of Alcohol-Containing Fuels from Sorbent Materials. Fuel and alcohol uptake and recovery analyses were undertaken for three alcohol-containing fuels and SiliaMetS[®] Diamine (Si-DIA) sorbent material. Gravimetric uptake was at room temperature and verified by GC. Thermal desorption was used to recover absorbed alcohol and fuel at the noted temperature ranges, and was verified by GC, except as noted.

Fuel	Alcohol	Alcohol			Fuel Mass Retained (g) ^(c)	Alcohol Recovered per Distillation Temperature Range ^(d)			Total Alcohol Recovered		Base Fuel Recovered (g)
		Available (g) ^(a)	Retained (g) ^(b)	Retained (%)		<100 °C (g)	100-120 °C (g)	120-150 °C (g)	(g)	(%) ^(e)	
A10	methanol	3.2	1.42	44.8	2.42	1.55			1.55	109	0.70
A20	methanol	4.8	0.60	12.6	2.15	0.09					0.45
	ethanol	1.6	0.17	10.6		0.01					
	alcohol ^(f)					0.60*	0.38*	0.10*	1.18	153	
E10	ethanol	3.2	0.66	21.0	2.11	0.05	0.04	0.06	0.15	22	1.18

(a) Ideal mass of alcohol available from fuel blend.

(b) Mass of alcohol retained based upon GC analysis of the residual fluid.

(c) Gravimetric measurement of the liquid-saturated sorbent material.

(d) Except as noted by an (*), mass of alcohol was confirmed by GC analysis of each distillate fraction.

(e) Values based upon a comparison of g Alcohol Recovered to g Alcohol Retained.

(f) Ethanol and methanol were not differentiated.

Table 4. Repeated Thermal Desorption of 10% Methanol-Containing Fuel (A10) from Sorbent Materials. Methanol and A10 fuel uptake and recovery analyses were undertaken using SiliaMetS[®] Diamine (Si-DIA) sorbent material. In this experiment, the sorbent material was saturated with neat methanol, the methanol thermally desorbed, and then the sorbent was repeatedly exposed to A10 fuel and the sorbed material recovered. Gravimetric uptake was at room temperature and verified by GC. Thermal desorption was used to recover absorbed methanol and fuel at the noted temperature ranges, and was verified by GC, except as noted.

Fuel	Cycle	Alcohol	Alcohol			Fuel Mass Retained (g) ^(c)	Alcohol Recovered per Distillation Temperature Range ^(d)			Total Alcohol Recovered		Base Fuel Recovered (g)
			Available (g) ^(a)	Retained (g) ^(b)	Retained (%)		<100 °C (g)	100-120 °C (g)	120-145 °C (g)	(g)	(%) ^(e)	
neat methanol	1	methanol		2.32		2.32	1.91*			1.91	82	--
	2	methanol	3.2	0.94	29.7	2.83	0.69			0.69	73	0.77
A10	3	methanol	3.2	0.91	28.8	1.71	1.03	0.38*		1.41	154	0.71
	4	methanol	3.2	1.00	31.6	2.68	0.73	0.39*	0.23*	1.35	135	0.62

(a) Ideal mass of alcohol available from fuel blend.

(b) Mass of alcohol retained based upon GC analysis of the residual fluid.

(c) Gravimetric measurement of the liquid-saturated sorbent material.

(d) Except as noted by an (*), mass of alcohol was confirmed by GC analysis of each distillate fraction.

(e) Values based upon a comparison of g Alcohol Recovered to g Alcohol Retained.

Table 5. Repeated Thermal Desorption of 10% Ethanol-Containing Fuel (E10) from Sorbent Materials. Ethanol and E10 fuel uptake and recovery analyses were undertaken using SiliaMets[®] Diamine (Si-DIA) sorbent material. In this experiment, the sorbent material was saturated with a neat ethanol, the ethanol thermally desorbed, and then the sorbent was repeatedly exposed to E10 fuel and the sorbed material recovered. Gravimetric uptake was at room temperature and verified by GC. Thermal desorption was used to recover absorbed ethanol and fuel at the noted temperature ranges, and was verified by GC, except as noted.

Fuel	Cycle	Alcohol	Alcohol			Fuel Mass Retained (g) ^(c)	Alcohol Recovered per Distillation Temperature Range ^(d)			Total Alcohol Recovered		Base Fuel Recovered (g)
			Available (g) ^(a)	Retained (g) ^(b)	Retained (%)		<100 °C (g)	100-120 °C (g)	120-145 °C (g)	(g)	(%) ^(e)	
neat ethanol	1			2.30		2.30	1.68*			1.68	73	--
	2	ethanol	3.2	0.16	5.1	2.25	0.22			0.22	136	1.05
E10	3	ethanol	3.2	0.47	15.0	2.19	0.09	0.50*		0.59	125	0.59
	4	ethanol	3.2	0.61	19.2	2.26	0.30	0.19*	0.20*	0.69	113	1.09

(a) Ideal mass of alcohol available from fuel blend.

(b) Mass of alcohol retained based upon GC analysis of the residual fluid.

(c) Gravimetric measurement of the liquid-saturated sorbent material.

(d) Except as noted by an (*), mass of alcohol was confirmed by GC analysis of each distillate fraction.

(e) Values based upon a comparison of g Alcohol Recovered to g Alcohol Retained.

Table 6. Repeated Thermal Desorption of 15% Methanol/5% Ethanol-Containing Fuel (A20) from Sorbent Materials. Methanol, ethanol, and A20 fuel uptake and recovery analyses were undertaken using SiliaMetS[®] Diamine (Si-DIA) sorbent material. In this experiment, the sorbent material was saturated with a neat methanol/ethanol blend (3:1 v/v), the methanol/ethanol thermally desorbed, and then the sorbent was repeatedly exposed to A20 fuel and the sorbed material recovered. Gravimetric uptake was at room temperature and verified by GC. Thermal desorption was used to recover absorbed alcohol and fuel at the noted temperature ranges, and was verified by GC, except as noted.

Fuel	Cycle	Alcohol	Alcohol			Fuel Mass Retained (g) ^(c)	Alcohol Recovered per Distillation Temperature Range ^(d)			Total Alcohol Recovered		Base Fuel Recovered (g)	
			Available (g) ^(a)	Retained (g) ^(b)	Retained (%)		<100 °C (g)	100-120 °C (g)	120-145 °C (g)	(g)	(%) ^(e)		
methanol ethanol blend (3:1 v/v)	1			2.20		2.20	1.73*			1.73	79	--	
						2.27	1.48						
		methanol	4.8	0.68	14.2		0.05					0.63	
		ethanol	1.6	-0.02	-1.1		0.01						
		alcohol ^(f)					0.79*			0.85	125		
	A20	3					2.26	1.45					
			methanol	4.8	1.11	23.4		0.06					0.48
			ethanol	1.6	0.09	5.8		0.01					
			alcohol ^(f)					0.91*	0.17*		1.14	95	
4							2.30	1.29					
		methanol	4.8	0.66	14.0		0.05						0.61
	ethanol	1.6	0.10	6.5		0.01							
	alcohol ^(f)					0.62*	0.15*	0.22*	1.05	138			

(a) Ideal mass of alcohol available from fuel blend.

(b) Mass of alcohol retained based upon GC analysis of the residual fluid.

(c) Gravimetric measurement of the liquid-saturated sorbent material.

(d) Except as noted by an (*), mass of alcohol was confirmed by GC analysis of each distillate fraction.

(e) Values based upon a comparison of g Alcohol Recovered to g Alcohol Retained.

(f) Ethanol and methanol were not differentiated.

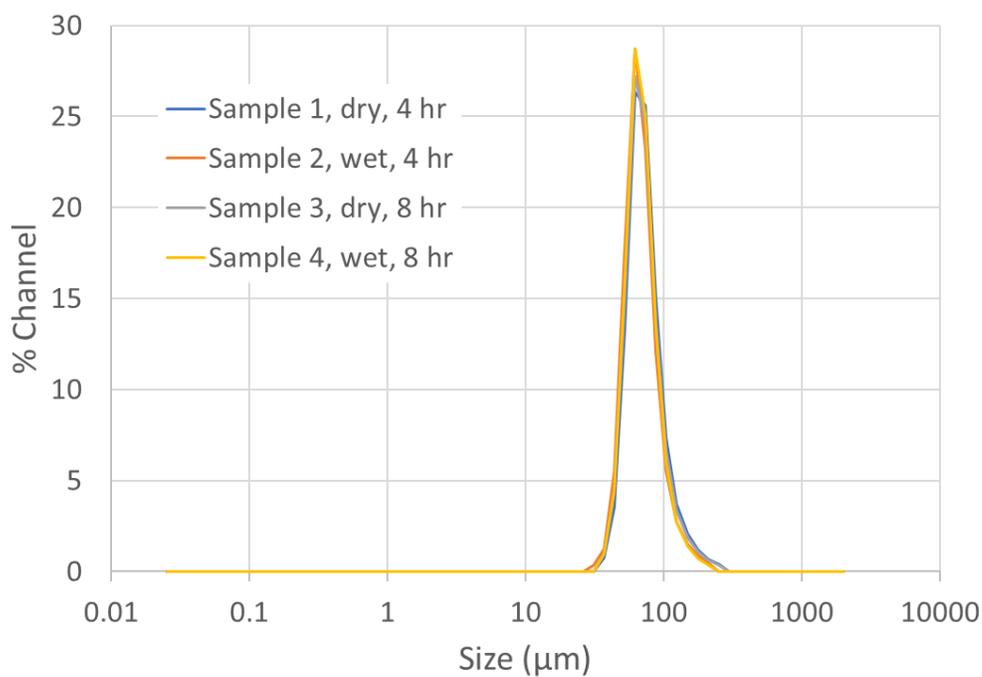
3.5 Vibration Testing

Vibration testing was used to determine the degree to which the particles attrite under vibration. Previous experience using similar particles under persistent vibration, suggested that attrition could occur over prolonged periods when packed in a loose form factor. In this case, the particles were packed tightly in a cartridge, as described in Section 2.8, to mimic a form factor that might be anticipated for automotive applications in a liquid flow-through cartridge.

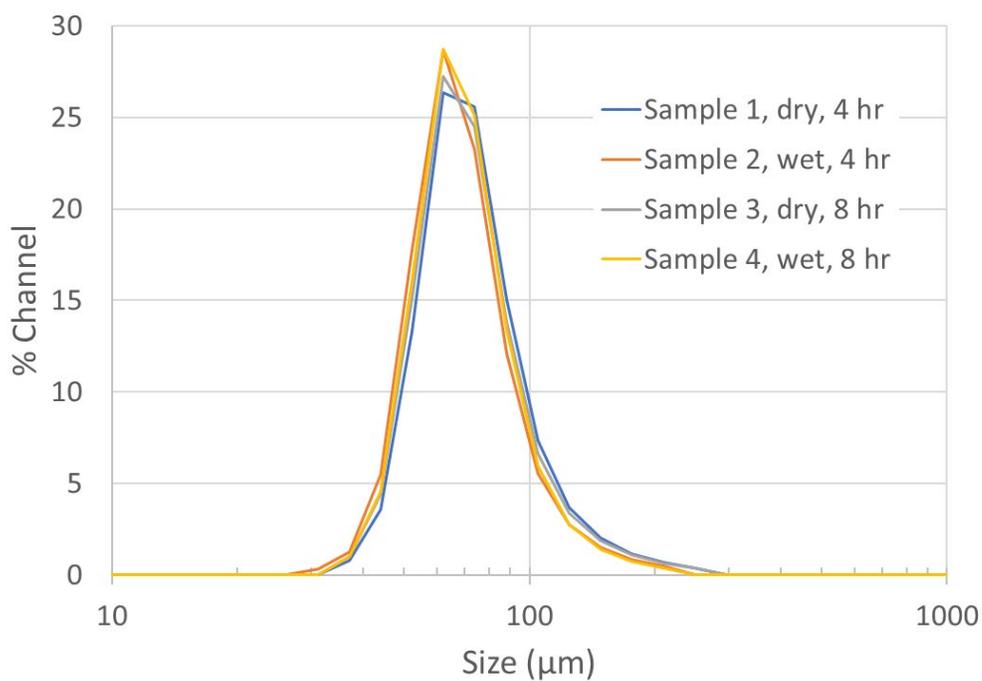
As described previously, the particles in the cartridge were saturated with water as the surrogate for gasoline. While gasoline would have been preferable, there was insufficient time during the project to accommodate the safety requirements at the test facility, so a non-flammable, innocuous fluid, water, was selected.

Figure 8 shows the particle size distribution versus size channels from the particle size analyzer. Figure 8(b) shows an enlarged region of Figure 8(a). Important to note is that the base particle size from SiliCycle is 40-60 μm , which corresponds fairly well to that shown in Figure 8. Limited time and resources precluded analysis of the original material, however, previous experience suggests that the particle size distribution is quite similar to that shown in Figure 8.

As shown in Figure 8, the test conditions did not appreciably affect the particles differently. These include testing the particles dry or wet with water, vibrated for periods of 4 or 8 hours, during which the temperature was cycled between $-40\text{ }^{\circ}\text{C}$ and $85\text{ }^{\circ}\text{C}$. This suggests that additional time or more extreme conditions would be required to show appreciable particle degradation.



a)



(b)

Figure 10. Laser diffraction particle size analysis of particles subjected to vibration testing. Samples 1 and 2 were subjected to 4 hours of vibration and samples 3 and 4 subjected to 8 hours of vibration. Samples 1 and 3 were dry, while samples 2 and 4 were immersed in water. (a) Full scale; (b) magnified. Original particle size per the manufacturer was between 40 and 63 μm . Samples appear to be uniformly unaffected by the conditions of this test.

3.6 System Design for Cycle Testing of SAMMS® Materials

One of the outstanding questions posed by the automobile manufacturers is how rapidly an alcohol can be removed from a fuel, and how long will the materials last before needing to be replaced. The period of performance under this LDRD was too short to purchase and assemble equipment to address these questions, however, a reliable design was developed and could be utilized for follow-on work. This task provided the basic design showing the necessary test equipment to answer those questions.

Several basic assumptions or criteria, described below, were made to provide a context for the scale and operation of the system. These were initial assumptions, and the design of the test system was meant to be flexible enough to accommodate changes that might be desired in the future.

Assumption and design criteria:

1. Ethanol can be thermally desorbed from SAMMS® materials in 2 steps: (1) one at 90-100 °C, and (2) at ~130 °C, which may or may not include use of a lower pressure to promote desorption. Other alcohols could also be tested; however, ethanol was of higher priority.
2. SiliCycle material would be the primary sorbent material tested. The material would be granular and have a grain size from 60 to 220 microns.
3. Alcohols would be physisorbed in the SAMMS® pores.
4. Approximately 2.5 grams of ethanol could be absorbed by 5 grams of EDA-SAMMS®
5. The system would target approximately 100 grams of sorbent
6. Gasoline-ethanol blends could range from E10 – E85
7. Up to 20 gallons of gasoline-alcohol blend could be tested at one time
8. Testing would evaluate a sorbent's alcohol capacity, (desorption) rate information, sorbent durability, product (alcohol) purity, i.e., address the amount of gasoline that was separated along with the alcohol, and investigate modes of sorbent regeneration.

With these assumptions and design criteria in mind, the basic system shown in the piping and instrumentation diagram (P&ID), Figure 9, was created. A larger version of the P&ID is provided in Appendix B. Figure 10 shows the basic construction and dimensions of the packed sorbent bed envisioned for this testing.

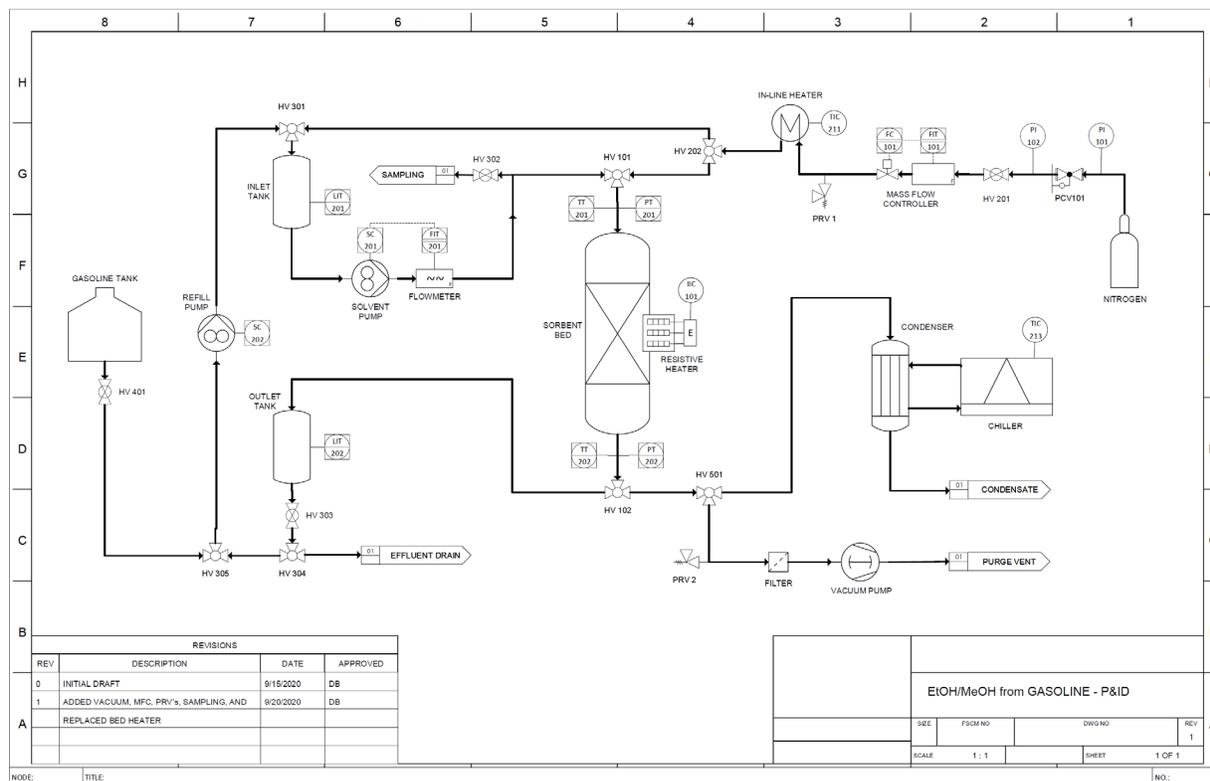


Figure 11. P&ID for Cycle Testing of SAMMS® Materials. The P&ID describes the basic system flows and measurement points for a fully instrumented test bed for evaluating materials used in alcohol separation from gasoline. (A larger version of the P&ID is in Appendix B.)

Brief description of major system components identified in Figure 9

GASOLINE TANK – Contains the feed fuel, isolated by HV 401.

HV 304 – 3-way valve that feeds the refill pump from either the OUTLET TANK or the GASOLINE TANK.

REFILL PUMP – Supplies fuel (fresh or recycled) to HV 301 and INLET TANK.

HV 301 – 3-way valve that provides fuel to the INLET TANK.

INLET TANK – Contains fuel that gets pumped into the SORBENT BED.

SOLVENT PUMP and FLOWMETER – Provides a metered quantity of fuel to the SORBENT BED.

HV 101 – Selects feed to the SORBENT BED as either fuel from the INLET TANK or heated N₂.

SORBENT BED – Houses the solids sorbent in a vertically-aligned packed-bed configuration configured for downward flow.

HV 102 – Directs flow from the SORBENT BED to either the OUTLET TANK or the CONDENSER and CONDENSATE collector.

RESISTIVE HEATER – Provides a means to heat sorbent in the SORBENT BED.

OUTLET TANK – Collects fuel (alcohol poor) that has passed through the SORBENT BED.

HV 302 – Downstream isolation valve for the OUTLET TANK.

NITROGEN, PCV101, HV 201, ROTAMETER, IN-LINE HEATER, and HV 202 – Provide a heated carrier gas for carrying sorbent desorption product to the CONDENSER.

CONDENSER and CHILLER – Condenses desorption product (alcohol) carried by the carrier gas coming out of the SORBENT BED.

Brief description of system operation:

Fuel charging – INLET TANK is charged with fuel from the GASOLINE TANK by the REFILL PUMP.

Fuel separation – The SOLVENT PUMP supplies a metered quantity of fuel flow through the SORBENT BED at operating temperature to the OUTLET TANK. This process can be repeated multiple times. Fuel can be sampled or drained from the OUTLET TANK via the Effluent Drain.

Product recovery – The SORBENT BED is heated by the RESISTIVE HEATER. Heated nitrogen is passes through the SORBENT BED and the effluent is directed to the CONDENSER and CONDENSATE collection.

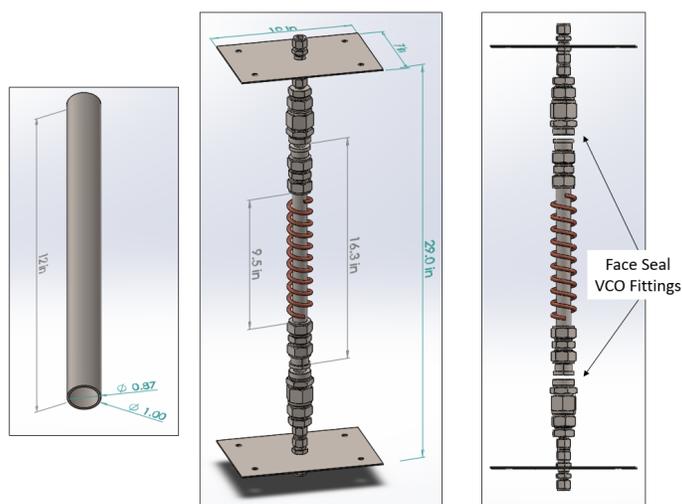


Figure 12. Sorbent Bed Design. The sorbent bed is a cylinder with fittings on either end with a resistive heating coil surrounding the portion of the cylinder containing the sorbent.

4.0 Conclusions

While the goals of this project were not fully realized, there are several notable conclusions that can be documented.

One of the four goals was clearly accomplished during this short period of performance. No trace chemicals were observed to be extracted from the sorbent materials. Aggressive conditions were used to provide the greatest probability of extracting contaminants. While these tests do not simulate the repetitive wear resulting from hundreds of absorption-recovery cycles, they suggest that if anything is extracted from the SAMMS[®] materials, the concentrations are very low, and would not be expected to build up. Further study in a benchtop system running the material through those cycles is needed to better assess the long-term behavior of the SAMMS[®]-based materials.

Similarly, vibration testing returned positive results that the silica-based substrate could handle the applied vibration, under conditions examined. These cycles fall short of longer-term testing in duration and did not use gasoline as a medium. While the gasoline is not expected to significantly change the coupling of the external vibration into the particles, a combination of vibration or shock conditions and chemical effects may elicit unexpected changes.

The other two goals were partially accomplished, although the results observed could benefit from additional absorption-recovery cycles of the material and a better means of testing to account for uptake and desorption conditions. These could likely be accomplished by using the benchtop testing unit.

From this work, it can be said that SAMMS[®] materials work well with methanol, yielding a higher sorption and recovery than was observed with ethanol. Ethanol requires higher recovery temperatures or the application of a vacuum swing, to enable lower recovery temperatures. The A20 mixed fuel and a failure to raise the temperature high enough to fully recover the associated ethanol made for complex results that are not fully understood. Additional work will provide a clearer understanding of how mixed fuels behave.

Of note and in partial accomplishment of the final project objective, limited testing to assess the rate of alcohol sorption suggests that very little contact time is needed for the materials to near their capacity when exposed to an alcohol-containing fuel. Since the sorption mechanism is via intermolecular forces (physisorption), it is expected that there is a definable time to reach equilibrium conditions. This time was not able to be measured as part of this study.

While aspects of the study were not fully accomplished, the achievements made have furthered the understanding of SAMMS[®] materials as a sorbent for separating alcohols from alcohol-containing gasoline. Scaling to a benchtop system will provide longer-term testing and more reliable answers than were possible with the limited testing conducted here.

5.0 References

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Appendix A – Intertek Vibration Testing Data

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BATTELLE MEMORIAL INSTITUTE (PNNI) VIBRATION TEST

SCOPE OF WORK:

CLIENT PROVIDED TEST PLAN WITH REFERENCE TO GMW 3172, SECTION 9.3.1 ON 4 GAS FILTERS

REPORT NUMBER:

104514626DET-001

ISSUE DATE:

02/01/2021

PAGES:

11

DOCUMENT CONTROL NUMBER

RT-L-AMER-005 (05/03/17)

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Vibration Test

BATTELLE MEMORIAL INSTITUTE (PNNI)
 Intertek Report No.: 104514626DET-001
 Client PO No.: 1006261995

BATTELLE

Gregory Coffey
 902 Battelle Blvd
 Richland WA 99352 USA
 Ph: 509-554-3506
 Email: greg.coffey@pnnl.gov

SAMPLE DISPOSITION:

At the conclusion of testing, the samples were returned to the client for further evaluation.

VIBRATION TEST:

Date Received: 01/08/2021
 Dates Tested: 01/27/2021 through 01/28/2021
 Location Tested: Intertek – Plymouth, Michigan

DESCRIPTION OF SAMPLES:

Part Description: Gas Filters
 Condition of Samples: DV

TEST EQUIPMENT:

ASSET #	DESCRIPTION	MANUFACTURER	MODEL #	SERIAL #	CAL DUE
375-311	ACCELEROMETER	PCB	J353B15	203301	04/17/2021
375-369	ACCELEROMETER	PCB	320C15	18078	03/08/2021
375-041	SIGNAL PROCESSOR	VIBRATION RESEARCH	VR9500	9513397E	03/16/2021
161-135.1	VIBE CONTROLLER COMPUTER	HEWETT PACKARD	PAVILION 400-034	MXU32703DC	RO*
160-211.1	CONTROLLER/CHAMBER	WATLOW	F4	016255 / N/A	03/20/2021
160-211P	ENVIRONMENTAL CHAMBER	THERMOTRON	F110CHV-30-30	10151	RO*
375-441	POWER AMPLIFIER	UNHOLTZ-DICKIE CORP	SA165F	5382	RO*
375-440	8000 LB SHAKER	UNHOLTZ-DICKIE CORP	H560B-16-3/ST	734	RO*

*RO = Reference only.



Vibration Test

BATTELLE MEMORIAL INSTITUTE (PNNI)

Intertek Report No.: 104514626DET-001

Client PO No.: 1006261995

TEST PROCEDURE:

Test Method:

Per Client Provided Test Plan with Reference to GMW 3172, Section 9.3.1

Number of Samples:

Four Gas Filters

- SN 001 (Dry – 4hr)
- SN 002 (Wet – 4hr)
- SN 003 (Dry – 8hr)
- SN 004 (Wet – 8hr)

The test samples were enclosed inside of steel tubing; two tubes contained test samples submerged in water and two tubes contained only the sample. All four tubes were then secured to a vibration exciter and subjected to a random vibration of 10-1000hz at an amplitude of 2Grms for 4 hours, Reference Table 1. Test samples were also subjected to temperature cycling, Reference Table 2.

After four hours had completed SN001 and SN002 were removed from testing and an additional 4 hours of vibration and temperature testing was performed on SN003 and SN004. This process was repeated for each of the X, Y, and Z Axis.

Frequency (Hz)	PSD (G ² /Hz)
10	0.1032
55	0.0336
180	0.0013
300	0.0013
360	0.0007
1000	0.0007

Table 1: Random Vibration Profile for Sprung Masses

Time (min)	Temp. (C°)
0	23
30	-40
75	-40
105	23
150	85
205	85
240	23

Table 2: Temperature Profile Used for Each Axis

ADDITIONAL TEST INFORMATION:

To help distinguish the axis orientation a black line was drawn on each sample. Horizontal lines indicate X Axis and vertical lines indicates Y Axis.

Green dots were marked on SN3 and SN4 in order to determine what samples needed to stay on test after first initial 4 hours were complete.



Vibration Test

BATTELLE MEMORIAL INSTITUTE (PNNI)

Intertek Report No.: 104514626DET-001

Client PO No.: 1006261995

ACCEPTANCE CRITERIA:

Functional status class shall be "A". Additionally, during visual inspection and dissection – DRBTR, there shall be no evidence of structural damage to the component.

RESULTS:

Client to determine final results.

APPENDICES:

Appendix A – Photographs

Appendix B – Vibration Data

Appendix C – Environmental Chamber Data



Vibration Test

BATTELLE MEMORIAL INSTITUTE (PNNI)
Intertek Report No.: 104514626DET-001
Client PO No.: 1006261995

REPORT AUTHORIZED PER ISO 17025:2005

When signed with physical or electronic signature, the contents of this report have been prepared and approved per Intertek's quality process in accordance with ISO 17025.

Jonathan Meszaros
Lead Technician

Joshua Campbell
Associate Engineer

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Vibration Test

BATTELLE MEMORIAL INSTITUTE (PNNI)

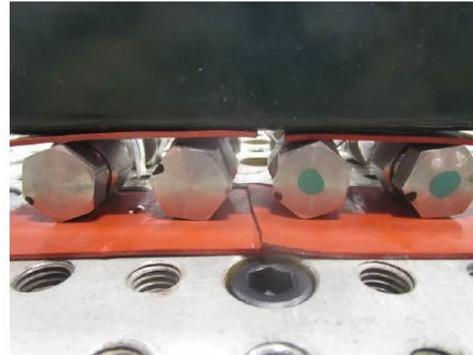
Intertek Report No.: 104514626DET-001

Client PO No.: 1006261995

APPENDIX A – PHOTOGRAPHS



Photograph 1: X Axis SN 001 – SN 004



Photograph 2: X Axis SN 001 – SN 004 Close Up



Photograph 3: X Axis SN 003 – SN 004



Photograph 4: X Axis SN 003 – SN 004 Close Up



Photograph 5: Y Axis SN 001 – SN 004



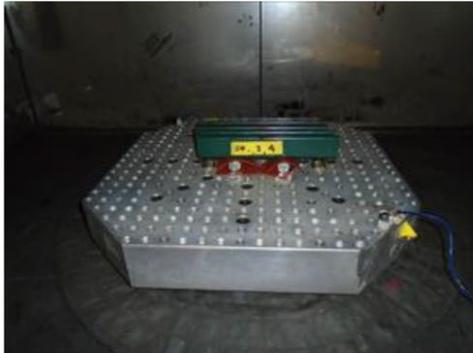
Photograph 6: Y Axis SN 001 – SN 004 Close Up



Vibration Test

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APPENDIX A – PHOTOGRAPHS (cont'd)



Photograph 7: Y Axis SN 003 – SN 004



Photograph 8: Y Axis SN 003 – SN 004 Close Up



Photograph 9: Z Axis SN 001 – SN 004



Photograph 10: Z Axis SN 003 – SN 004



Vibration Test

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APPENDIX B – VIBRATION DATA

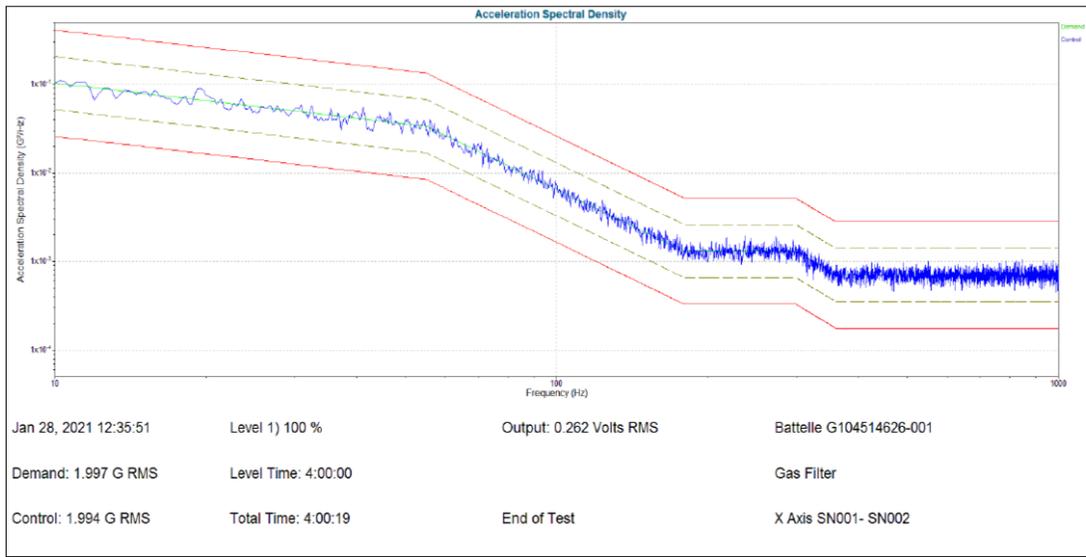


Figure 1: X Axis SN 001 – SN 002

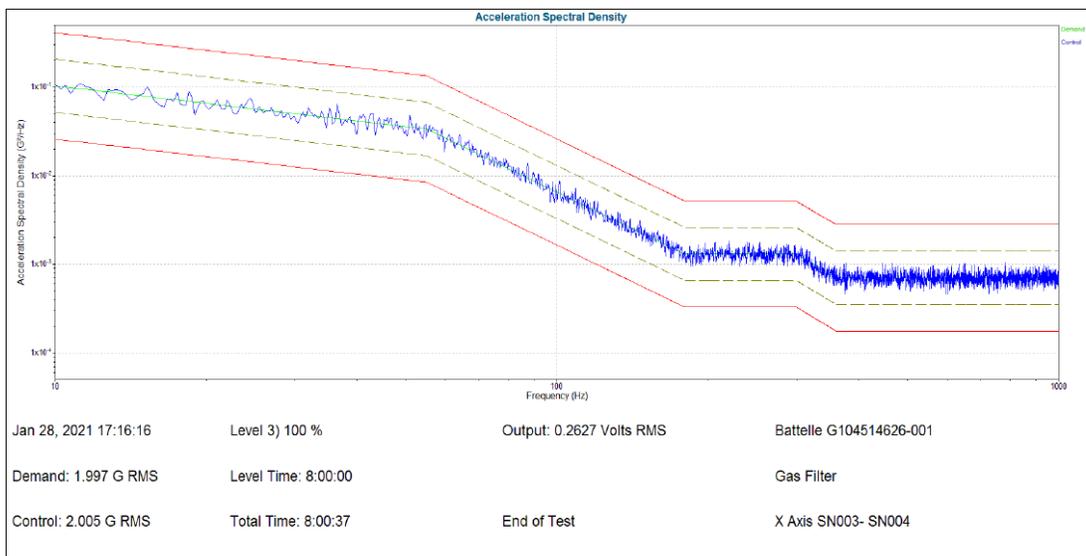


Figure 2: X Axis SN 003 – SN 004



Vibration Test

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APPENDIX B – VIBRATION DATA (cont'd)

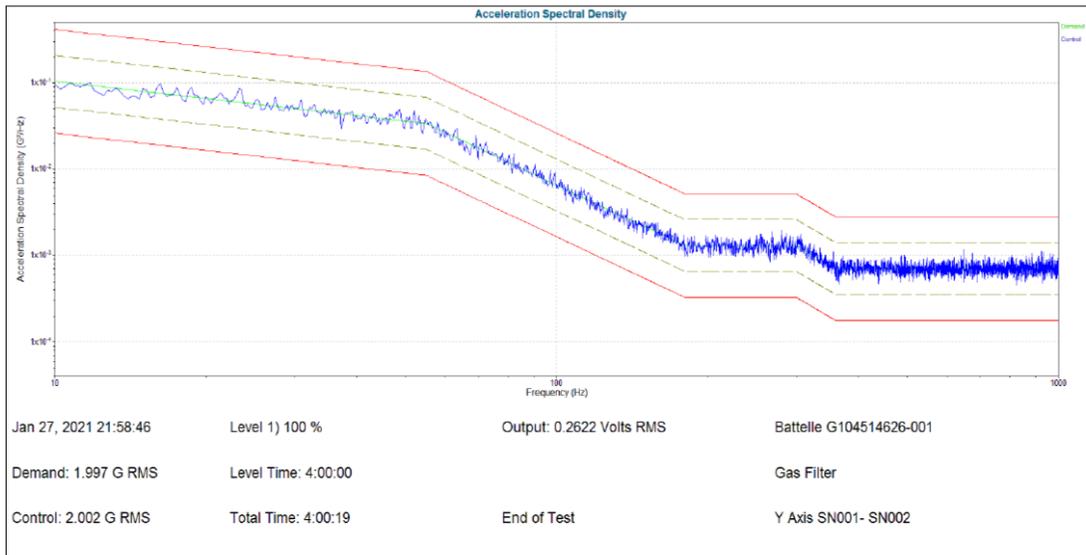


Figure 3: Y Axis SN 001 – SN 002

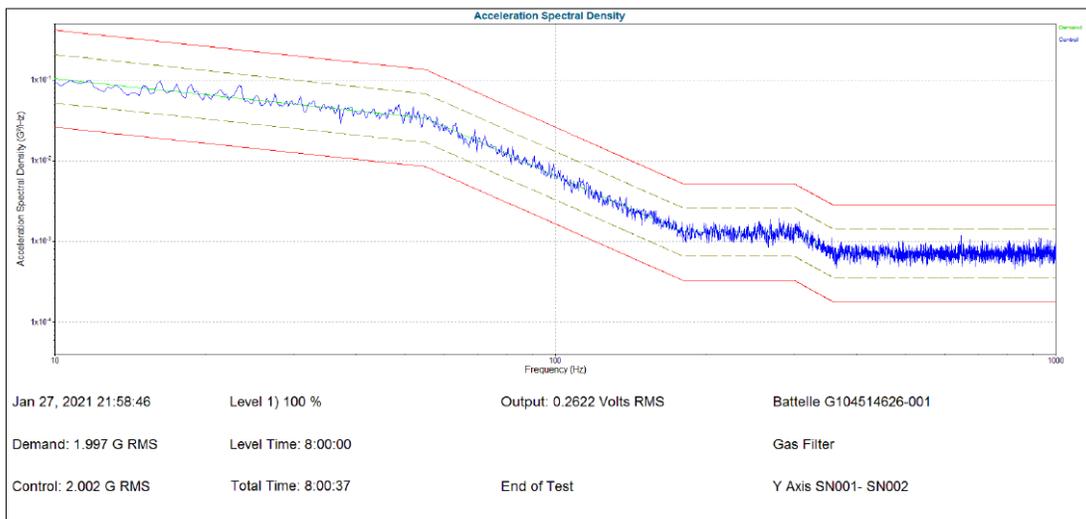


Figure 4: Y Axis SN 003 – SN 004



Vibration Test

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APPENDIX B – VIBRATION DATA (cont'd)

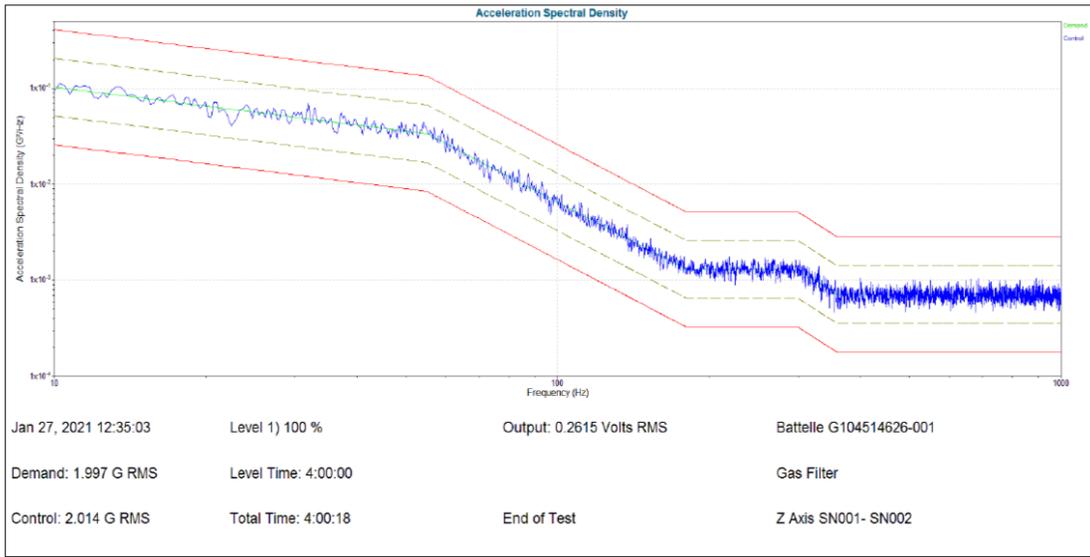


Figure 5: Z Axis SN 001 – SN 002

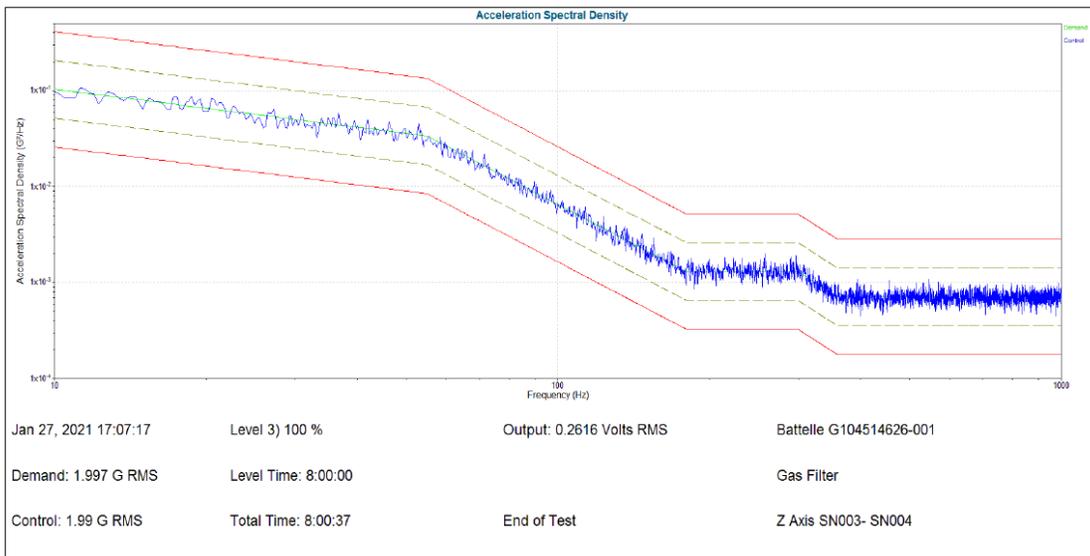


Figure 6: Z Axis SN 003 – SN 004



Vibration Test

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APPENDIX C – ENVIRONMENTAL CHAMBER DATA

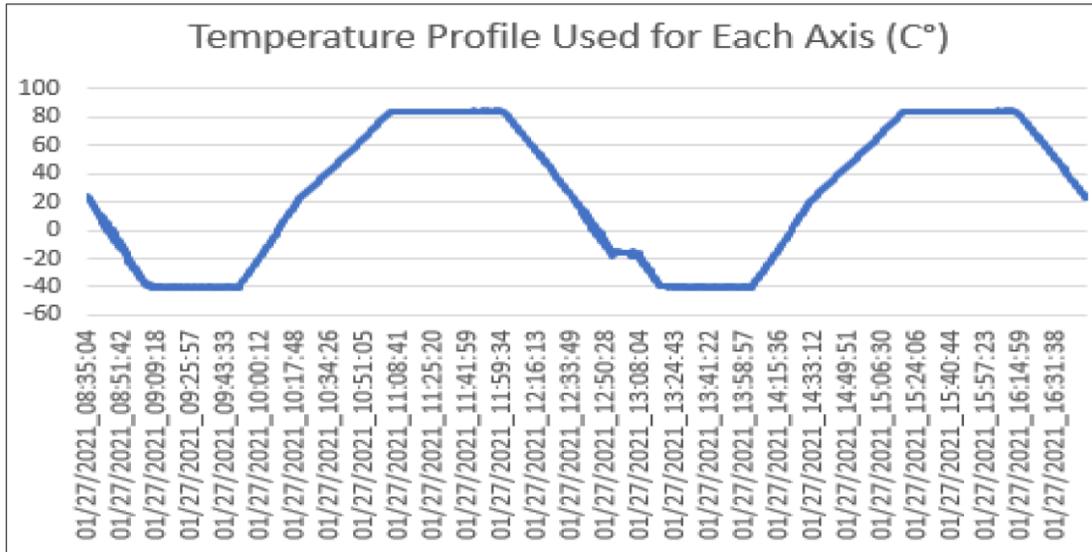
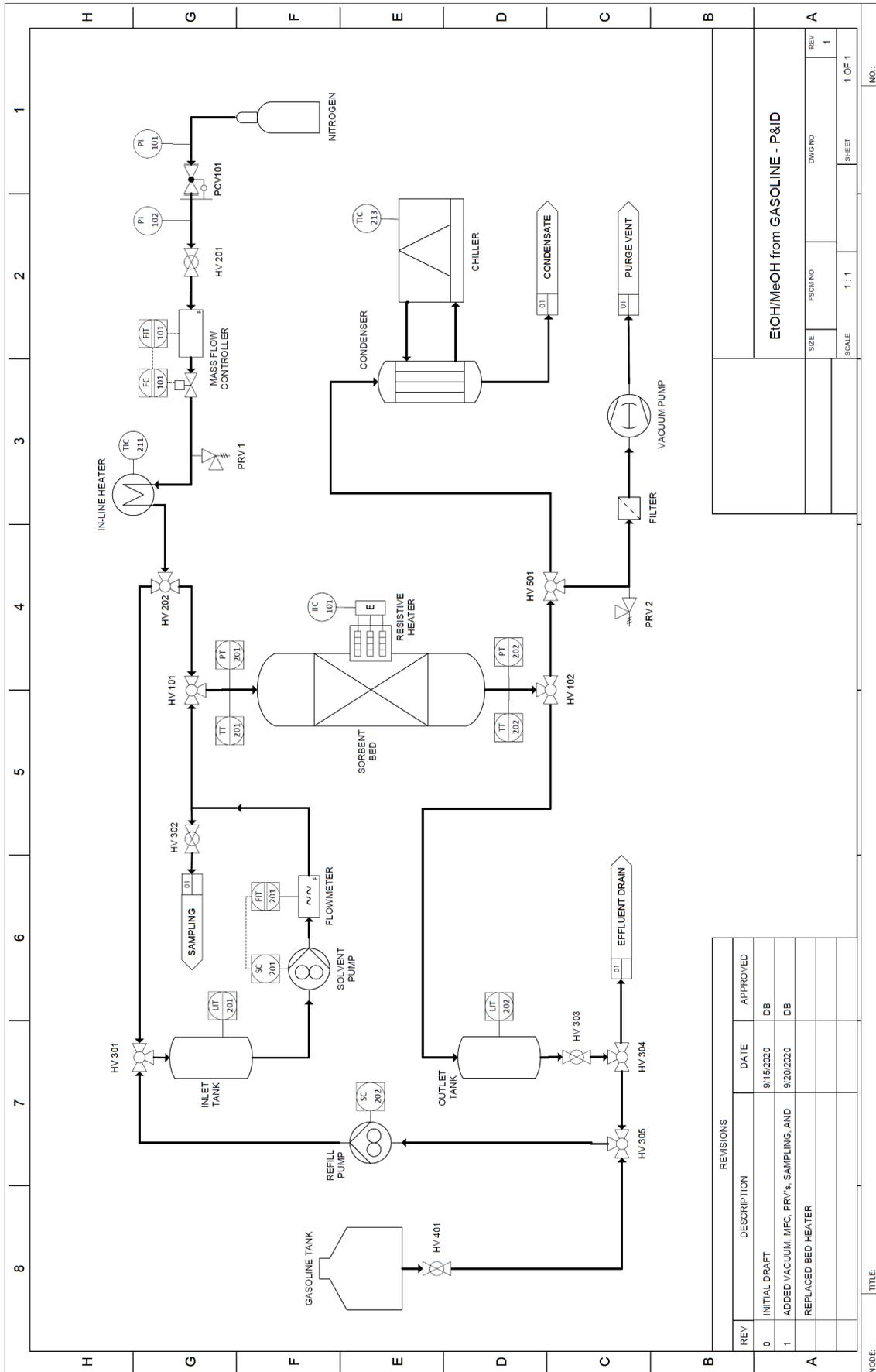


Figure 7: Environmental Chamber Data

Appendix B – P&ID for Cycle Testing of SAMMS[®] Materials



REV	DESCRIPTION	DATE	APPROVED
0	INITIAL DRAFT	9/15/2020	DB
1	ADDED VACUUM, MFC, PRV's, SAMPLING, AND REPLACED BED HEATER	9/20/2020	DB

EtOH/MeOH from Gasoline - P&ID			
SIZE	FSR/NO	DWG/NO	REV
SCALE	1:1	SHEET	1 OF 1
NO.:			NO.:

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