Extension - Upgrading Methane Using Ultra-Fast Thermal Swing Adsorption

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Abstract

The purpose of this project is to develop a cost effective technology for upgrading coal mine methane to natural gas pipeline quality. Nitrogen rejection is the most costly step with conventional technology and emerging competitive technology. Significant cost reductions to this step will allow for the cost effective capture and utilization of this otherwise potent greenhouse gas. The proposed approach is based on the microchannel technology platform that Velocys is developing to commercialize compact and cost efficient chemical processing technology. For this application, ultra fast thermal swing adsorption is enabled by the very high rates of heat transfer enabled by microchannels.

Natural gas upgrading systems have six main unit operations: feed compressor, dehydration unit, nitrogen rejection unit, deoxygenator, carbon dioxide scrubber, and a sales compressor. The NRU is the focus of the development program, and a bench-scale demonstration has been initiated. The Velocys NRU system targets producing methane with greater than 96% purity and at least 90% recovery for final commercial operation. A preliminary cost analysis of the methane upgrading system, including the Velocys NRU, suggests that costs below \$2.00 per million (MM) BTU methane may be achieved. The cost for a conventional methane upgrading system is well above \$2.30 per MM BTU, as benchmarked in an Environmental Protection Agency study.

Initial performance results for the Velocys TSA technology were promising. Velocys has also completed initial discussions with several prospective users of the technology and received positive market feedback. Some of the factors that create an attractive opportunity for the technology include the sustained high prices for natural gas, the emerging system of carbon credits, and continued focus on reducing coal mine emissions. While market interest has been confirmed, improvements and optimization are necessary to move the technology to a point that will enable commercial investment in the technology scale-up. In particular, prospective industry collaborators are interested in seeing validation that the technology can meet real-world conditions, including handling impurities, meeting purity and recovery targets (which requires low dead volume), and meeting cost and manufacturability goals.

In this quarter, a review of structured adsorbents has been completed. A short list of options, including a promising material available from Oak Ridge National Laboratory, with high effective thermal conductivity has been identified.

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Executive Summary

The purpose of this project is to develop a cost effective technology for upgrading coal mine methane to natural gas pipeline quality. Nitrogen rejection is the most costly step with conventional technology and emerging competitive technology. Significant cost reductions to this step will allow for the cost effective capture and utilization of this otherwise potent greenhouse gas. The proposed approach is based on the microchannel technology platform that Velocys is developing to commercialize compact and cost efficient chemical processing technology. For this application, ultra fast thermal swing adsorption is enabled by the very high rates of heat transfer enabled by microchannels

The objective of the project extension over 24 months is to further evaluate the microchannel technology under real world processing conditions. Five main objectives are proposed:

- Identify one or more commercial absorbents that can meet the purity and recovery requirements for pipeline specifications
- Demonstrate that the absorbents can operate with real feed mixtures of coal mine methane streams
- Demonstrate that the bench-scale adsorber meets the purity, recovery, and durability requirements
- Confirm manufacturability of absorber units and identify critical development needs
- Show that the technology meets industry's economic targets for capital and operating costs

During the initial phase of the project, a number of key technical accomplishments were completed including:

- The thermal swing adsorption project demonstrated sufficient initial adsorbent differential capacity for methane and nitrogen on microporous carbon. The best differential capacity was at 100 psig between 40°C and 60°C, where roughly 10 mg/gm methane and less than 1 mg/gm nitrogen were observed.
- A preliminary system and component design were performed to understand the requirements for process economics.
- An initial bench-scale demonstration was completed with a single cylindrical channel device, where a thermal swing time of 10 seconds for a bed differential temperature of 20°C was measured.
- A feed stream of 70% methane and 30% nitrogen was separated and purified to a mixture of 92% methane and 8% nitrogen with the use of an interstage purge to flush out the large dead volume on the test system.

The status of all tasks is listed below:

- Task 1: Evaluate improved and optimized adsorbents – *ongoing*
 - The initial literature review of structured adsorbents has been completed
 - One promising candidate with a high effective thermal conductivity has been selected for additional study.
- Task 2: Evaluate feed mixtures with major contaminants – *pending*

- Task 3: Demonstrate the bench-scale adsorber with reduced system dead volume and with a real feed mixture and improved adsorbent – *pending*
- Task 4: Develop preliminary manufacturing plan for full-scale microchannel units and identify critical development needs – *pending*
- Task 5: Update system design and cost based on thermal integration with coal-mine methane upgrading plants – *pending*
- Task 6: Commercialize Technology – *pending*
- Task 7: Project Management – *ongoing*

Actual and Budgeted Cumulative Project Costs

Figure 1. Project spendplan

The project has started slowly and remains below budget.

Experimental

The project has initiated with an investigation into improved adsorbent options for use in the nitrogen rejection application. The evaluation has expanded in breadth to include structured adsorbents, including foams, felts, cloths, and the like.

Important parameters for consideration in evaluating new materials include:

- Thermal conductivity: to swing the bed faster
- Heat capacity: to reduce the amount of energy required to swing the bed
- Capacity: increase the uptake of methane
- Cost: integrate cost competitive and manufacturable structures into microchannel devices

Measurement of Effective Thermal Conductivity:

A simple and direct method has been implemented for measuring the thermal conductivity of both structured adsorbents and small volume powder beds. The test method is based on an ASTM standard, “Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus,” C 518-04.

The test apparatus is most amenable to the measurement of materials with volumes in the range of 2 to 5 cc. The test device consists of wide diameter stacked, cylindrical material volumes positioned between a heat source and a heat sink, per the ASTM recommendations. The assembly is maintained at constant and controlled temperatures. A variac-controlled heater serves as the heat source; a circulating water bath maintains the lower temperature of the system – such that a known heat flux is pushed through the sample to be evaluated. Based on a simple one-dimensional heat transfer model, the effective thermal conductivity is calculated as the heat flux (W/cm^2) multiplied by the thickness of the sample (in cm) and divided by the measured temperature differential across the sample (in C). The resulting numerical value is modified to fit the conventional SI thermal conductivity units of $\text{W}/\text{m}\cdot\text{K}$.

The proper axial alignment of all components and parallel positioning of all material layers is critical to achieving uni-axial heat transfer for accurate measurements. Proper selection of reference material thickness and thermal conductivity allows minimal heat loss from the equipment and easy control of temperature gradients across the assembly. All components are relatively easily stacked and positioned on one another through the use of centering/alignment rings.

For powder testing, an even distribution and a flat contact surface are enabled by repeated shaking of the sample chamber. If necessary, sample powder beds can be compressed prior to testing using a 1-in die press. Fabric samples were tested both perpendicularly to the weave and in the fiber direction. The effective thermal conductivity in the fiber direction was measured by rolling the fabric into short tubes, placing them in a circular plastic retainer, and carefully cutting these into planar disks. Under these circumstances, the plastic retainer serves as the sample chamber and is constrained between two reference disks.

The device has been designed based on available industry test standards for thermal conductivity measurement. The following two references were specifically consulted for the design:

- ASTM, “ Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus,” C 518-04.
- Salmon, D., “Thermal conductivity of insulations using guarded hot plates, including recent developments and sources of reference materials,” Meas. Sci. Technol. 12, R89–R98, 2001.

Results and Discussion

Several parameters are under consideration for an optimized adsorbent for the thermal swing application:

- Thermal conductivity: Carbon powder has a thermal conductivity on the order of 0.4 W/m-K. A target value of 1 W/m-K is sought to facilitate a thermal swing time near 1 second. A larger system temperature differential for heat transfer may enable the use of a lower thermal conductivity material at short cycle times.
- Heat capacity: The reported heat capacity for the granular carbon adsorbent is 1260 J/kg-K. Reduced values of heat capacity for structured adsorbents will reduce the amount of energy required to thermally swing the adsorbent bed and reduce the overall capital and operating cost of the system.
- Capacity: The available differential capacity for methane versus nitrogen will drive the overall size of the unit and the attainable purity per pass.
- Cost: It is targeted to select an adsorbent material that is no more than 10% of the overall capital cost of the adsorption hardware.

Thermal Conductivity

The measured effective thermal conductivity for several evaluated samples is listed in Table 1.

Table 1: Results of Effective Thermal Conductivity Measurements

	<i>thermal conductivity (W/m-K)</i>
<i>Powder</i>	
Calgon Activated Carbon, 80/100 mesh	0.18
<i>Foam</i>	
15904 Plate, BS PocoFoam Graphite Foam	166
<i>Fabric, perpendicular to the fiber direction</i>	
Carbon Weave Fabric, Calgon FM10	0.053
<i>Fabric, fiber direction</i>	
Carbon Weave Fabric, Calgon FM10	0.21
Carbon Weave Fabric, Calgon Sateen	0.23

Literature Review

A review of the literature was conducted to evaluate additional options for structured adsorbents. The results are tabulated in Table 2.

Table 2: Literature Review of Structured Carbon Adsorbents

Material	Source and status	Citation	Effective Thermal Conduction (W/m·K)	Porosity	CH₄ reported Capacity (mg/g)	Heat Capacity (J/g/°C)
Carbon Composite Molecular Sieve; formed to any geometry	Oak Ridge National Laboratory, demonstrated at development scale	1	0.0422-0.0863 W/m-K near ambient conditions; > 0.4 W/m-K after high temperature heat treatment	Densities = 0.19-0.27 g/cm ³	N/R	684-2150 J/kg K
Carbon fiber molecular sieves	Oak Ridge National Laboratory, demonstrated at development scale	2	N/R	Pore volume = 0.5-1.0 cm ³ /g	Evaluated for air separation, analogies to other separations; at 100 psig, O ₂ = 50 mg/gm N ₂ = 35 mg/gm; CO ₂ = 300 mg/gm	N/R
Carbon Monoliths based on C fibers	Oak Ridge National Laboratory, demonstrated at development scale	5	N/R	Pore volume = 0.56 - 1.09 cm ³ /g Pore diameter = 2.06 - 2.68 nm Surface Area = 1494 - 2860 m ² /g	at 20 C, CH ₄ Capacity of >150V/V (gas to adsorbent)	N/R
Carbon Fiber Cloth	Material tested from American Kynol (ACF-5092-20)	8	N/R	Pore diameter <20 Å Surface Area = 2000-2500 m ² /g	Capacity range from 100 to 400 mg/g for volatile carbon adsorbates	estimated 0.725 J/g°C (graphitic carbon)

Material	Source and status	Citation	Effective Thermal Conduction (W/m·K)	Porosity	CH4 reported Capacity (mg/g)	Heat Capacity (J/g/°C)
Molecular Sieve Carbon Membranes	National Carbon Institute, Spain ; deposition or growth of active carbon on substrate	11	N/R	Pore diameter = <4Å	permeance not capacity reported	N/R
Carbon Fiber Composites (contiguous fibers or monolith structure)	LexCarb prepared carbon fibers; MAST carbon prepared carbon monoliths	15	N/R	Densities = 0.15 - 0.44 g/cm ³ Pore Volume = 0.295 - 0.516 cm ³ /g Surface Area = 700 - 1151 m ² /g	hexane 200 mg/gm near ambient	N/R
Carbon Monoliths based on C fibers	Oak Ridge National Laboratory, demonstrated at development scale	17	range from 0.3 to 1.1 W/m-K at 100 C depending upon material density	Pore diameter = >50 µm Pore volume = 0.5-1.0 cm ³ /g Surface Area = 1000-2000 m ² /g Densities = 0.15-0.8 g/cm ³	at 100 psia, 40 mg/gm CH ₄ and 200 mg/gm CO ₂	N/R
Carbon foam	Oak Ridge National Laboratory, demonstrated at development scale	18	> 100 W/m/K	Pore diameter = 93 µm, Density = 0.54 g/cm ³	N/R	N/R
Carbon foam Conoco-derived	Oak Ridge National Laboratory, demonstrated at development scale	19	40-135	Pore diameter = 60-90 µm Density = 0.2 - 0.6 g/cm ³	N/R	N/R

Material	Source and status	Citation	Effective Thermal Conduction (W/m-K)	Porosity	CH4 reported Capacity (mg/g)	Heat Capacity (J/g/°C)
Carbon foam: from aluminosilicate templates or surfactant stabilized silica templates	Seoul National University in development	22	N/R	Pore diameter = 3.5 nm or 10 nm depending on synthesis technique, uniform pores	N/R	N/R
Carbon foam ARA24-derived	Oak Ridge National Laboratory, demonstrated at development scale	19	50-150	Pore diameter = 275-350 μ m Density = 0.2 - 0.6 g/cm ³	N/R	N/R
Carbon Fiber Cloth	Masters thesis evaluating commercial materials from American Kynol; Taiwan Carbon; Actitex, Calgon Carbon; Carbon Resources	24	0.12 (for ACC-5092-20)	Pore diameter 6.1 - 14.4 A Pore Volume = 0.364 - 1.059 cm ³ /g Surface Area = 730 - 1994 m ² /g Density = 1.96 - 2.31 g/cm ³ Porosity = 12.5 - 81.6 %	N/R	Graphitic Carbon from literature cp (J/gK) = 0.0004T + 1.2438
Carbon fiber-cloth (ACFC-20)	University of Illinois, experimental measurements of commercial fiber	25	N/R	Pore diameter = 13 A; Density = 480 mg/cm ³	2 to 10 mg/gm acetone	N/R

Material	Source and status	Citation	Effective Thermal Conduction (W/m·K)	Porosity	CH4 reported Capacity (mg/g)	Heat Capacity (J/g/°C)
Carbon monolith Binder: PVA, HAS, PR, TF, WSC, ADH	University of Alicante, Spain; developed activated carbon monoliths from powders with different binders	26	N/R	Density from 0.4 to 1 g/cm ³ depending upon binder selection	capacity similar to original powder carbon sample; 60 mg/gm at 100 psig	N/R
Activated Carbon Discs	University of Alicante, Spain; developed discs by pressing powders with phosphoric acid	27	N/R	Density = 0.71 - 0.98 g/cm ³	130 - 150 V/V of methane	N/R
Carbon Fiber Composite Molecular Sieve	Oak Ridge National Laboratory, demonstrated at development scale	28	N/R	Density = 0.16 - 0.18 g/cc	20 mg/gm for CO ₂	N/R
Graphite nanofibers	Northeastern University; experimental development stage	29	N/R	Pore diameter = 0.34 nm *noted that the H ₂ expanded the fibers during testing, but they returned at the end of testing.	Adsorbed > 40 wt% of H ₂	N/R
Carbon foam	Texas A&M thesis	34	N/R	Density = 0.272, 0.480 g/cm ³	N/R	N/R

Material	Source and status	Citation	Effective Thermal Conduction (W/m-K)	Porosity	CH4 reported Capacity (mg/g)	Heat Capacity (J/g/°C)
Molded Activated Carbon Sheets made from wood pulp	Hokkaido University, Japan	37	N/R	Pore diameter = < 5 nm Surface Area = 1290 - 1560 m ² /g	I ₂ Adsorption Capacity = 1100 - 1360 mg/g	N/R

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Conclusions

Work is accelerating to evaluate structured carbon as an adsorbent in microchannel devices for use in nitrogen rejection. Contact has been initiated with several vendors, including a plant visit, to explore the experimental evaluation of a structured adsorbent for differential capacity under the real world operating conditions.

Acronyms and Abbreviations

Btu	British thermal unit
GHG	greenhouse gas
gm	gram
GWP	global warming potential
HPBV	high-performance butterfly valve
kg	kilogram
mg	milligram
MMSCFD	million standard cubic feet per day
MW	megawatts
NRU	nitrogen rejection unit
psig	pound per square inch gauge
SLPM	standard liters per minute
TSA	thermal swing adsorption

Public Recognition of the Project

A publication has been accepted for oral presentation at both the AIChE Spring meeting in Orlando Florida and AICHEMA 2006 in Frankfurt Germany on the use of thermal swing adsorption in a microchannel TSA unit for nitrogen rejection.