Upgrading Methane Using Ultra-Fast Thermal Swing Adsorption

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Project No. 41905

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Abstract

The purpose of this project is to design and demonstrate an approach to upgrade low-BTU methane streams from coal mines to pipeline-quality natural gas. The objective of Phase I of the project was to assess the feasibility of upgrading low-Btu methane streams using ultra-fast thermal swing adsorption (TSA) using Velocys' modular microchannel process technology.

The project is on schedule and under budget. For Task 1.1, the open literature, patent information, and vendor contacts were surveyed to identify adsorbent candidates for experimental validation and subsequent demonstration in an MPT-based ultra-fast TSA separation for methane upgrading. The leading candidates for preferential adsorption of methane over nitrogen are highly microporous carbons. A Molecular Gate[™] zeolite from Engelhard Corporation has emerged as a candidate. For Task 1.2, experimental evaluation of adsorbents was initiated, and data were collected on carbon (MGN-101) from PICA, Inc. This carbon demonstrated a preferential capacity for methane over nitrogen, as well as a reasonable thermal swing differential capacity for a 90% methane and 10% nitrogen mixture. A similar methane swing capacity at 2 psig was measured. The mixture composition is relevant because gob gas contains nearly 85% methane and must be purified to 97% methane for pipeline quality.

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Executive Summary

The purpose of this project (41905) is to design and demonstrate an approach to upgrade low-Btu methane streams from coal mines for subsequent deployment as pipeline-quality natural gas. This approach is based on applying Velocys' modular microchannel process technology (MPT) to achieve ultra-fast thermal swing adsorption (TSA). The ultra-fast TSA project is a two-phased, 18-month effort. The objective of Phase I is to assess the technical and market feasibility of an MPT-based TSA approach for upgrading low-Btu methane streams. Below are the tasks included in Phase I.

- Task 1.1: adsorbent ranking *complete*
- Task 1.2: adsorbent testing *ongoing*
- Task 2.1: process design *initiating*
- Task 2.2: component design
- Task 3: cost and feasibility analysis
- Task 4: proof-of-principle demonstration.

Highlights of the first quarter effort are that

- The project was under budget. Overall budget is on track, but spending will increase next quarter to test additional adsorbents.
- The project is on schedule with completion of the first two milestones. Tasks for the second quarter milestones have been initiated.
- Velocys issued a press release on January 14 announcing the inception of this DOE-funded project.

Technical progress to date includes

- Completed absorbent ranking from technical and patent literature and vendor supplied information (Task 1.1)
- Began adsorbent validation experiments (Task 1.2)
- Demonstrated satisfactory adsorbent performance in initial tests.

For Task I.1, the open literature (Appendix I), patent information (Appendix II), and vendor contacts were surveyed to identify adsorbent candidates for experimental validation and subsequent demonstration in a MPT-based ultra-fast TSA separation for methane upgrading. The leading candidates for preferential adsorption of methane over nitrogen are highly microporous carbons. One candidate for preferential adsorption of nitrogen over methane has emerged, a Molecular GateTM zeolite from Engelhard Corporation.

For Task 1.2, evaluation of adsorbents has begun and data are being collected on the first adsorbent, a carbon (MGN-101) from PICA, Inc. The carbon sample demonstrates preferential capacity for methane over nitrogen, as well as a reasonable thermal swing differential capacity (15 mg/gm methane and less than 2 mg/gm nitrogen between 6 C

and 40 C at both 2 psig and 100 psig.) for a 90% methane and 10% nitrogen mixture. A similar methane swing capacity at 2 psig was measured, while the nitrogen swing capacity dropped below 1 mg/gm. The mixture composition is relevant as gob gas contains nearly 85% methane and must be purified to 97% methane to be pipeline quality.

At the end of the first quarter of FY04, approximately \$30,000 had been spent. The project is under budget, but an increased spending rate is anticipated in the second quarter of FY04 as the number of adsorbents tested increases. The project is on schedule with completion of the first–quarter milestones:

- Completed adsorbent ranking
- Initiated adsorbent validation experiments.

Progress is ongoing for the second-quarter milestones:

- Complete adsorbent validation experiments
- Complete conceptual system process design.



On January 14, 2004, Velocys issued a press release announcing that DOE was funding this project to apply MPT to "recover methane that today often emits to the atmosphere as a harmful greenhouse gas." The press release was sent to Business Wire and distributed to several relevant media channels including Coal, Mining & Minerals, and Government Agencies & Technology. The press release was also sent directly to a small number of local business publications. At least one local business newsletter, *Business First*, issued an article on the announcement. See Appendix III for a copy of the press release.

Velocys, Inc. Cumulative Budget to Actual for MONTANA

Experimental

Task 1.1 Adsorbent Ranking

Task Objective

The goal of the adsorbent ranking task was to identify at least one adsorbent that is sufficient for demonstrating the ultimate performance and cost advantage of an MPT-based TSA process for upgrading coal mine gob gas to pipeline quality. In particular, the objective is to identify adsorbents for the most challenging separation, nitrogen from methane. Identification of an adsorbent that preferentially adsorbs nitrogen over methane was sought, although preferential adsorption of methane over nitrogen also could be acceptable. The final goal of this task was to identify the adsorbent that could most easily (rather than perfectly or optimally) be used to move forward. Concurrent improvements to selected adsorbents or the identification of new adsorbents is expected to occur in parallel with the remaining tasks as time and budget allow.

Adsorbent Criteria

Successful adsorbents for deployment in an MPT-based TSA process must possess the following attributes:

- High preferential capacity for either methane or nitrogen
- High differential capacity for either methane or nitrogen over a modest temperature range (5 C to 40 C expected, to be confirmed in Task 2.1)
- High attrition resistance during modest thermal swings
- Stability to constituents found in gob gas and corresponding cyclic regenerability as required, e.g., low levels of water must be reversibly removed periodically to maintain a sufficient working capacity.
- Reasonable cost.

The literature primarily contained information pertaining to preferential and differential capacity of either methane or nitrogen in single feed experiments as a function of temperature. There were fewer references citing results with mixed feed operation. This criterion is deemed the most important to identify an adsorbent candidate for a successful demonstration of MPT-based TSA processing for cost-effective methane upgrading.

Very little information was found regarding adsorbent stability to thermal swings because the vast majority of adsorbents are commercially used in pressure swing absorption (PSA) not TSA application. There was little information on stability to other gob gas constituents (O_2 , CO_2 , and H_2O). For many adsorbents, including the carbon family, carbon dioxide (CO_2) was more strongly adsorbed than methane. For most adsorbents, water is very strongly adsorbed – but reversibly so, when regenerated at temperatures of a few hundred degrees Celsius. No exotic adsorbents were identified as potential candidates, and thus reasonable costs are expected.

Preferential Methane Adsorption

The vast majority of all cited literature describes adsorbents with a preferential affinity for methane over nitrogen. Calculations and reasonable technical assumptions were made as necessary to create a standardized comparison basis for capacity (mg adsorbate per gm adsorbent).

Table 1 ranks journal literature for adsorbents based on methane capacity at low pressure (around 1 atm). Note that all carbon adsorbents are highlighted in blue, the zeolites in orange, and the remaining adsorbents in contrasting colors. These adsorbents at low pressure have the lowest capacity, as expected, and represent a system configuration where minimal feed compression is required for an ultimate system. These adsorbents also reflect options for capturing methane from coal mine ventilation gas. Adsorbent capacity ranges from 10 to 20 mg/gm of methane at low pressure.

Table 2 ranks journal literature for adsorbents based on methane capacity at modest pressure (around 100 psig). These adsorbent options have higher capacity and represent a system that would require modest compression of the feed prior to the TSA process. The resulting feed would then be subsequently compressed to pipeline conditions (around 500 psig). Adsorbent capacity ranges from 50 to 80 mg/gm near 100 psig.

Table 3 ranks journal literature for adsorbents based on methane capacity at higher pressure (around 300 psig). These adsorbent options have the highest capacity, but would also require more feed compression prior to the TSA separation process. Adsorbent capacity for methane near 300 psig has been reported as high as 150 mg/gm.

Table 4 ranks patent literature for adsorbents based on either nitrogen or methane capacity. The primary adsorbent for preferential methane adsorption is carbon. The primary adsorbent for preferential nitrogen adsorption is a zeolite.

The selection of the operating pressure will be made in Task 2.1 based on performance (purity, recovery rate, and reliability) and cost.

Preferential Nitrogen Adsorption

One candidate emerged from the literature review that demonstrated preferential nitrogen adsorption over methane. The Molecular GateTM technology from Engelhard Corporation is based on specially synthesized barium exchanged titano-silicate molecular sieve that create a pore opening of roughly 3.7 angstroms. This pore opening allows nitrogen (molecular diameter of 3.6 angstroms) to enter and adsorb while excluding methane (molecular diameter of 3.8 angstroms). For this adsorbent, significant co-adsorption of carbon dioxide (molecular diameter of 3.4 angstroms) is also reported. Only one reference (M70, patent 5,989,316) presented capacity data without requiring additional

assumptions – roughly 10 mg/gm of nitrogen versus 2 mg/gm of methane at 25 C and 1 atm is reported.

		CH4	N2		
Adsorbent name	Reference	(mg/gm)	(mg/gm)	T in C	P (atm)
Activated carbon (G2X7/12					-
from Takeda Industries)	M24	27	12	0	1
Activated carbon sheet					
(carbonized foam)	M42	25			1
Anderson AX-21 (activated					
carbon)	M27	24	14	25	1
Activated carbon (Mega	M4.0	00		05	4
	M18	20		25	1
Activated carbon (G2X7/12 from Takeda Industries)	M24	10	10	25	1
Activated carbon	MQ	19	10	20	1
Calgon BPL (carbon)	M27	10	6	20	1
Activated carbon (A35/4)	M43	16	0	20	1
NaX zeolite	M2	15		0	1
Activated carbon (Calgon					
Carbon BPL)	M18	15		25	1
H-ZSM-5-30	M35	11	7	40	1
AX-21 (activated carbon)	M8	10		23	1
BPL (activated carbon)	M8	10		23	1
CVD modified Na-A zeolite	M13	10		30	1
5A zeolite	M30	10	10	23	1
K04 (activated carbon)	M6	8		25	1
Zeolite (5A)	M9	8		25	1
Pyrolized polyvinylidene					
chloride (carbon)	M27	8	6	25	1
Pyrolized furfuraldehyde	1407	0	6	05	4
		8	0	20	1
	N/1	52	3.5	40	1
NaY zeolite	M2	5	0.0	25	1
Aluminum pillared clay	MZ	48		0	1
AIPO4-11	M1	4.6	1 1	40	1
AIPO4-18	M1	27	1.7	40	1
MCM-41	M34	2	,	30	1
Fe-substituted kaolinite	M10	1.4	1.8	25	1
Vulcan carbon	M41	0.5	0.25	20	1

Table 1. Adsorbents for methane and nitrogen at low pressure – open literature

Table 2 . Adsorbents for methane and nitrogen at modest pressure (~ 100 psig) – open
literature

		CH4	N2		
Adsorbent name	Reference	capacity (mg/gm)	capacity (mg/gm)	T in C	P (nsia)
AX 21 (activated carbon)	M20	(iiig/giii) 95	(iiig/giii) 60	25	100
Activated carbon	M36	80	<u> </u>	20	100
Activated carbon	10130	00	50	20	100
Carbon Ax-21)	M18	70		25	100
Anderson AX-21	M27	70	60	25	100
Pyrolized polyvinylidene chloride (carbon)	M27	65	55	25	100
AX-21 (activated carbon)	M8	60		23	100
NaX zeolite	M2	50		25	100
Calgon BPL (activated carbon)	M27	50	40	25	100
Activated carbon (A35/4)	M43	50		20	100
Activated carbon	M9	48		26	100
K04 (activated carbon)	M6	40		25	100
BPL (activated carbon)	M8	40		23	100
Activated carbon (Calgon		10		05	400
Carbon BPL)	M18	40		25	100
Activated carbon	M22	40	34	45	120
5A zeolite	M30	35	40	23	90
zeolite (5A)	M9	32		25	100
NaY zeolite	M2	30		25	100
Pyrolized furfuraldehyde	M27	30	28	25	100
Carbon molecular sieve 5A	M47	20	20	20	100
12X Molecular Sieve	M21	30	20	20	100
AS Activisted Carbon		25		30	100
		25		35	100
	10134	12		30	100
Vulcan carbon	M39	2	1	25	100

		CH4 capacity	N2 capacity		
Adsorbent name	Reference	(mg/gm)	(mg/gm)	T in C	P (psig)
Activated carbon (Mega					
Carbon Ax-21)	M18	150		25	300
AX-21 (activated carbon)	M8	140		23	300
Anderson AX-21	M27	140	115	25	300
Pyrolized polyvinylidene					
chloride	M27	90	100	25	300
AS Activated Carbon	M21	70		35	300
Calgon BPL (activated carbon)	M27	70	70	25	300
Activated carbon (Calgon Carbon BPL)	M18	65		25	300
NaX zeolite	M2	60		25	300
BPL (activated carbon)	M8	60		23	300
NaY zeolite	M2	55		25	300
13X Molecular Sieve	M21	50		35	300
Pyrolized furfuraldehyde	M27	40	50	25	300
MCM-41	M34	24		30	300

Table 3. Adsorbents for methane and nitrogen at high pressure (300 psig) – open literature

Adsorbent name	Patent Reference	CH4 capacity (mg/gm)	N2 capacity (mg/gm)	T in C	P (atm)
Li exchanged zeolites	M52		34	23	1
Zeolite-2	M53		30	20	1
Engelhard Ba- ETS-4 (at 30 seconds)	M70	2	11	25	1
Engelhard Ba- ETS-4 (at 10 minutes)	M70	7	11	25	1
Activated carbon (bituminous and subbituminous coal)	M54	8		25	1
Engelhard CTS-1 or Ba-ETS4 (density estimated at 0.5g/cc)	M63	4	10	27	27
Nusorb-A14	M65	178	10	25	34
Westvaco SN20- A1	M65	196		25	34
Microporous carbon	M66	13		10	1

Table 4. Adsorbents for methane and nitrogen separation – patent literature

Competitive Adsorption in Mixtures

Much of the reported data was collected as single-component isotherms. Several references discussed multi-component behavior based on fractional mixtures of methane and nitrogen. For all classes of adsorbents (carbons, reference M22; zeolites, reference M30; aluminophosphates, reference M1; and H-ZSM-5, reference M35), the capacity of methane relative to nitrogen increases with increasing concentration of methane. Methane out competes nitrogen for sites. This bodes well for the target application of upgrading gob gas (roughly 80% methane) to pipeline quality (roughly 97% methane).

Recommended Adsorbents from Industrial Partner

Our industrial partner, Joe D'Amico of D'Amico Technologies, has a long and successful history in the industry with developing and deploying systems for upgrading natural gas. He has recommended several adsorbents, including activated carbon from PICA, Barnaby-Sutcliffe, and Westvaco. In addition, he has recommended a zeolite from Davison. At present, Mr. D'Amico has provided samples from Barnaby-Sutcliffe and we have procured samples from PICA. We anticipate samples from Westvaco and Davison to arrive in early February.

Selection of Adsorbents for Experimental Validation

The following adsorbents have been selected for testing in Task 1.2.

- Activated Carbon
 - o PICA
 - Barnaby-Sutcliffe
 - o AX-21 microporous carbon
 - Carbonized foams
- Zeolites
 - o Davison
 - Na-X substituted zeolite (from reference M2)
 - Li-exchanged zeolite (from reference M52)
- Molecular Gate from Engelhard if samples will be made available for preferential nitrogen adsorption

Task 1.2 Adsorbent Validation

Task Objective

The objective of this task is to identify an adsorbent candidate suitable for initiating a conceptual system design and a subsequent bench-scale demonstration. The testing program evaluates capacity and differential capacity as a function of temperature, pressure, and inlet composition. Testing will be complete by the end of February, where an adsorbent that is sufficient, but perhaps not optimal, will be selected for additional study.

Adsorbent Testing

The test system is designed to measure capacity as a function of temperature, pressure, and composition for different solid granulated forms of adsorbents. The system includes an adsorbent bed with heat exchanger to maintain isothermal operation during experiments (as shown in Figure 1).

The adsorbent bed consists of an inner tube with 1/2" outside diameter (OD) housed within an outer tube of 3/4" OD. The length of the adsorbent bed is 6", for a typical loading of 5 to 7 grams of adsorbent (based on 0.35 to 0.5g/mL density). For the current tests, 5.4 grams of adsorbent were loaded. A 50/50 mix of glycol and water heat exchange fluid flows through the annulus at 4 gallons/min. The heat exchange fluid temperature can be varied from 0C to 45C.

The system (as shown in Figure 2) also includes a feed line and a purge gas line that can each be electronically turned off and on. The feed line can add a custom mix of methane and nitrogen. The purge line is used to "clean" or desorb the solutes between experiments.



Figure 1. Adsorbent testing apparatus. Process gases flow downward through the (vertically mounted) adsorbent bed in the center tube and heat exchange fluid flows co-currently in an outer annulus to maintain near isothermal operation.



Figure 2. Adsorbent testing system flow diagram.

The feed gases are metered separately through Brooks mass flow controllers, mixed, and can either be fed directly to the sample analysis line or fed through a small preheater and into the adsorption bed. At the start of each test while argon is fed to the adsorption bed, the feed gases are routed via 3-way valves to the analyzer system. After leaving the adsorption bed, gases can then be sent to either the bypass vent line or to the sample analysis line which includes an Omega mass flow meter, a Raytech Nitrogen analyzer and a California Analytical Instruments $CH_4/CO/CO_2$ analyzer. As shown in Figure 2, the flow exiting the flowmeter in the sample analysis line is split to feed the nitrogen and $CH_4/CO_2/CO$ analyzers in parallel.

The procedure for running each experiment is

- 1) Grind adsorbent particles with mortar and pestle or small ball mill.
- 2) Sieve the particles to recover the 212- to 425-micron particle size fraction (40-70 mesh).
- 3) Load the test apparatus with a known weight of undesiccated adsorbent (5-7 gms) from the above particle size fraction.
- 4) Calibrate flow controllers and analyzers against known standards.
- 5) Purge the bed with argon at expected total feed flow rate until no other gases are seen by the analyzers.
- 6) Set system pressure with the BPR (either 0 psig or 100 psig).
- 7) Set system temperatures by adjusting the temperature of the chiller and the pre-heater.
- 8) Set feed flow rates and bypass the adsorbent bed, sending them to the analyzer to check composition.
- 9) Send feed flows to vent and purge (argon) flow to the adsorbent bed and sample analysis line until no more methane or nitrogen is detected in outlet stream.
- 10) Simultaneously start the feed to the adsorbent bed and stop the purge gas (argon) flow at time t0 by opening the valve solenoid-1 and closing solenoid-2.
- 11) Record the measured outlet flow rates and compositions as a function of time via LabView program.
- 12) After steady-state is established, stop test by closing solenoid-1 and opening solenoid-2 (flow purge gas over the bed to remove the sorbed solutes).

Once the testing is complete, the data can be collected at any given time interval, generally 1-second increments are used. Future adsorbent validation tests will likely use 0.5-second intervals for better response resolution and improved accuracy. The data collection system records the time when the solenoids are switched giving an exact start time to the test. The system dead time (about 1 second at 2 psig and 7.3 seconds at 100psig) and the response delay of the analyzers must be taken into account when calculating breakthrough time and capacity.

Calculating Capacity

Adsorbent capacity was calculated for each test condition as the cumulative milligrams of each component fed to the system less the cumulative milligrams of each component exiting the system per gram of adsorbent.

$$capacity = \frac{\sum_{j=1}^{n} (mg \ i \ in - mg \ i \ out)_{j}}{grams \ of \ adsorbent}$$

where mg i in or out is the mass of component i entering or exiting the bed at time increment j (with a total of n time increments). Note that the dead time, or the time required for the process flows to first reach the adsorbent bed is not included in the calculation. The mass of each component i (CH_4 and N_2) entering and leaving the adsorbent bed was calculated at each time interval j and summed over all time periods from the end of the dead time to the time when each component ceased adsorbing according to the following equations:

$$\begin{split} mg \ i \ in_{j} &= SLPM \ i \ in_{j} \cdot \left(\frac{1 \ min}{60 \ sec}\right) \cdot \left(\frac{1 \ mmol \ i \ / \ min}{0.0224 \ SLPM \ i}\right) \cdot \left(\frac{MW_{i} \ mg \ i}{mmol \ i}\right) \cdot time \ interval_{j} \\ mg \ i \ out_{j} &= SLPM \ out_{j} \cdot \left(\frac{1 \ min}{60 \ sec}\right) \cdot \left(\frac{1 \ mmol \ / \ min}{0.0224 \ SLPM}\right) \cdot y_{i,j} \left(\frac{MW_{i} \ mg \ i}{mmol \ i}\right) \cdot time \ interval_{j} \end{split}$$

where SLPM is the flow rate (total or component i) converted to standard liters per minute (standard conditions being 0 °C and 1 atm), MW_i is the molar mass of component i, $y_{i,j}$ is the mole fraction of component i at time j, and time interval_j is the time increment at time j in seconds. The stream composition ($y_{i,j}$) exiting the bed at time j was assumed to be the mole fraction measured in the sample analysis line analyzers after a delay period had elapsed. This delay period (about 0.5 to 1 second longer for CH₄ than for N₂) was the average time needed for the gas to flow from the bed exit to the analyzer, given the average outlet flow rate during that time. Because of the large proportion of process gases which were adsorbed, variations in the outlet flow rate were very significant and the calculated delay period was substantial (typically 7-13 seconds).

Results and Discussion

Task 1.1 Adsorbent Ranking

The open literature, patent information, and vendor contacts have been surveyed to identify adsorbent candidates for experimental validation and subsequent demonstration in a MPT-based ultra-fast TSA separation for methane upgrading. The leading candidates for preferential adsorption of methane over nitrogen are highly microporous carbons. One candidate for preferential adsorption of nitrogen over methane has emerged—Molecular GateTM zeolite from Engelhard Corporation.

Task 1.1 is complete with the selection of eight adsorbents for additional study. The adsorbents include four carbons, three zeolites, and the preferential nitrogen adsorbent from Engelhard— if this material will be shared. However, periodic searches of the literature will continue at a low level to identify new adsorbent findings.

Task 1.2 Adsorbent Validation

Experimental evaluation of adsorbents has been initiated and data collected on the first adsorbent, activated carbon (MGN-101) from PICA, Inc. The carbon sample demonstrates preferential capacity for methane over nitrogen, as well as a reasonable thermal swing differential capacity (15 mg/gm methane and less than 2 mg/gm nitrogen between 6 C and 40 C at both 2 psig and 100 psig.) for a 90% methane and 10% nitrogen mixture. Surprisingly, a similar methane swing capacity at 2 psig is measured, while the nitrogen swing capacity drops below 1 mg/gm. The mixture composition is relevant because gob gas contains nearly 85% methane and must be purified to 97% methane for pipeline quality. These initial results show that high capacity adsorbents are available.

The results of adsorption capacity testing for the PICA Carbon adsorbent are shown in Tables 5 through 6 and in Figures 3 through 8. The capacity data (Tables 5 through 6) show the expected increase in capacity with increasing mole fraction of a given component. For the most part, the data show the expected trends of increasing capacity with decreasing temperature and increasing pressure. However, a few data points (especially nitrogen) do not show the expected decrease in capacity as temperature is increased. This is attributed to errors in the nitrogen analyzer measurements, and possibly errors in the outlet flow meter readings (as it was calibrated using the inlet composition, while the actual composition varied throughout the testing). The experimental changes suggested in the next section are intended to improve the accuracy of the capacity estimation in future tests.

Temp (C)	Pressure (psig)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	2	100	900	5.8	20.8
6	2	500	500	21.2	9.2
6	2	900	100	32.2	1.3
23	2	100	900	4.1	19.1
23	2	500	500	14.2	10.2
23	2	900	100	21.6	2.6
40	2	100	900	2.7	11.5
40	2	500	500	10.0	5.6
40	2	900	100	16.4	1.8

Table 5. PICA Carbon MGN-101, capacity as a function of temperature and mixture composition near 1 atm

Table 6. PICA Carbon MGN-101 capacity as a function of temperature and mixture composition near 100 psig

Temp (C)	Pressure (psig)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	100	100	900	16.4	64.8
6	100	500	500	70.1	21.1
6	100	900	100	94.2	5.3
23	100	100	900	12.7	37.8
23	100	500	500	55.4	26.8
23	100	900	100	94.4	18.6
40	100	100	900	9.6	53.6
40	100	500	500	41.9	23.8
40	100	900	100	79.5	2.9





Figure 3. Outlet molar flow rate of nitrogen and methane for equimolar feed mixture, 6 C and 2 psig. Dead time is 1second.



Pica 6 C 0psig 900sccm CH4, 100sccm N2

Figure 4. Outlet molar flowrate of nitrogen and methane for 90% methane and 10% nitrogen at 6 C and 2 psig. Dead time is 1 second.

Pica 6C 100psig 500sccm CH4, 500sccm N2



Figure 5. Outlet molar flowrate of nitrogen and methane for equimolar mixture at 6 C and 100 psig. Dead time is 7.3 seconds.



Pica 6C 100psig 900sccm CH4, 100sccm N2

Figure 6. Outlet molar flowrate of nitrogen and methane for 90% methane and 10% nitrogen at 6 C and 100 psig. Dead time is 7.3 seconds.

Pica 40C 100psig 900sccm CH4, 100sccm N2



Figure 7. Outlet molar flowrate of nitrogen and methane for 90% methane and 10% nitrogen at 40 C and 100 psig. Dead time is 7.3 seconds



Pica 6C 100psig 500sccm CH4, 500sccm N2

Figure 8. CH₄ and N₂ concentrations at the exit of the adsorbent bed (left axis) and total outlet flow rate (right axis) for equimolar inlet mixture at 6 C and 100 psig. Dead time is 7.3 seconds.

Experimental System Upgrades

During the initial data collection phase, experimental issues were identified for future upgrading. One specific issue raised that may impact the quality of the first data set collected is the response factor of the methane and nitrogen sensors. The cited vendor response times were less than one second. Observed response times and lag was found to be strongly dependent upon the effluent flowrate and increased to tens of seconds to achieve full response for very low flowrates. In the next set of tests an additional flow line will be added upstream of the sensor to boost the total flow and reduce the sensor response lag. Another specific issue identified was the dependence of the mass flow meter calibration on gas composition. A composition dependent calibration curve will be developed for future tests.

Conclusions

Early data based on the PICA MGN-101 carbon is encouraging. The differential swing capacity for methane approaches 15 mg/gm between 6 C and 40 C, while it is less than 1 mg/gm for methane under the same conditions at 2 psig pressure and a 90% methane/10% nitrogen feed mixture. All future adsorbents will be benchmarked against these values.

Tier one testing of adsorbents will be completed for the at least eight adsorbents identified from Task 1.1. Each adsorbent will be tested under the same conditions to identify a preferred candidate.

Modifications to the experimental system will be initiated to reduce the effect of the sensor response lag. An added flow line will be added to boost the total flow preceding the sensor. The impact of the added flow will be subtracted from the data before analysis.

Tier two adsorbent testing will be initiated as part of Task 3 (Cost and Feasibility Assessment) to study potential kinetic limitations. A small test device will be constructed and tested to study the impact of reduced differential and swing capacity during short cycles (1 to 10 seconds).

Plans for the second quarter of FY04 are as follows:

- Complete testing of seven remaining adsorbent candidates (Task 1.2)
- Select adsorbent to serve as basis of conceptual system and process design in Tasks 2.1 and 2.2.
- Initiate and complete system design study (task 2.1)
- Initiate component design (task 2.2)
- Initiate Task 3, tier 2 adsorbent testing to identify kinetic limitations if any.
- Plan for Task 3, tier 3 adsorbent testing for material stability to thermal swings and potential poisons

Acronyms

- BPR back pressure regulator
- MPT microchannel process technology
- OD outside diameter
- PSA pressure swing adsorption
- psig pound per square inch gauge
- TSA thermal swing adsorption

Appendix I–Adsorbent Ranking Open Literature Reference List

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Appendix II–Adsorbent Ranking Patent Literature Reference List

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Appendix III – Velocys Press Release



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Facsimile

FOR IMMEDIATE RELEASE

Contact: Jeff McDaniel 614-733-3300

Velocys/DOE Project Aims to Reduce Greenhouse Gas Emissions While Recovering Methane Energy Streams

PLAIN CITY, Ohio, Jan. 13, 2004 – A government-supported project is now under way at Velocys, Inc. to apply the company's microchannel process technology (MPT) to recover methane that today often emits to the atmosphere as a harmful greenhouse gas.

The project is funded with a \$400,000 grant from the U.S. Department of Energy (DOE). The advanced technology under development is targeted for use in coal mines, landfills, natural gas fields and other industries trying to cope with waste methane streams.

"Traditionally, operators of mines and landfills have recovered only a fraction of these methane streams because they contain too many impurities and are too expensive to cleanse," said Wayne Simmons, Chief Executive Officer of Velocys. "Using MPT in a rapid-swing thermal adsorption system promises to separate a purified methane stream far more economically than current approaches. That would yield valuable energy from an otherwise wasted resource, and at the same time benefit the environment by avoiding emissions of a potent greenhouse gas."

"Solving the methane problem for coal mines and landfills would open economic avenues for upgrading or recovering methane from other sources," Simmons said, "including nitrogen contaminated, geological natural gas (methane is the main component of natural gas)."

When commercially deployed, MPT-based separation/purification systems have the potential to reduce U.S. annual greenhouse gas emissions by 23.5 billion equivalent kilograms of carbon dioxide, and to enable the cost-effective annual recovery of 3.5 trillion cubic feet of natural gas, which is equivalent to about 550 million barrels of crude oil.

About Velocys

Velocys is an advanced technology company developing and deploying microchannel process technology (MPT) to solve some of the chemical and energy industries' most daunting processing challenges. Founded by Battelle Memorial Institute in 2001, the company has advanced MPT well beyond the concept stage with the design, construction, scale-up and testing of MPT devices for various chemical and petroleum processes. Velocys is headquartered near Columbus in Plain City, Ohio. For further information call 614-733-3300 or visit <u>www.velocys.com</u>.

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