Upgrading Methane Using Ultra-Fast Thermal Swing Adsorption

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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 is to assess the technical feasibility and cost of upgrading low-Btu methane streams using ultra-fast thermal swing adsorption (TSA) using Velocys' modular microchannel process technology. The objective of Phase II is to demonstrate the process at the bench-scale.

The project is on schedule and on budget. For Task 1.2, experimental validation of 6 adsorbents (three microporous carbons and three zeolites) was completed. A microporous carbon is selected as appropriate to preferentially adsorb methane and reject nitrogen in a Velocys ultra-fast TSA system. A conceptual system design and analysis was completed in Task 2.1 based on the adsorbent performance results. The system has six main unit operations: feed compressor, dehydration unit, nitrogen rejection unit, deoxygenator, CO₂ scrubber, and a sales compressor. The nitrogen rejection unit (NRU) is the focus of the development program and was further studied within the system to identify performance targets. The Velocys NRU system targets producing methane with greater than 96% purity and at least 80% recovery for initial market entry and greater than 90% for final commercial operation. A preliminary cost analysis of the methane upgrading system, including the Velocys NRU, suggests that costs below \$2.00 per 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 EPA study.

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Executive Summary

The purpose of this project (41905) is to develop 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 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 a Velocys TSA approach for upgrading low-Btu methane streams. The status of all tasks is listed below:

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

Highlights of the second quarter effort are as follows

- The project is on budget and on schedule.
- Tasks for the third quarter milestones have been initiated.
- Velocys presented project results at the NETL annual review

Technical progress to date includes

- Completed adsorbent selection for demonstration, a microporous carbon from either Calgon Corporation or Barnaby-Sutcliffe are sufficient for further analysis
- Completed system design, including the initial cost and feasibility assessment

For Task 1.2, six adsorbents were tested (3 carbon and 3 zeolite) for differential capacity of methane and nitrogen as a function of temperature, pressure, and feed composition. In Task 2.1, the initial system design was completed, and includes a feed compressor, dehydration unit, nitrogen rejection unit, deoxygenation unit, carbon dioxide scrubber, and a sales compressor.

Progress is ongoing for the third-quarter milestones:

- Complete component design
- Complete cost and feasibility assessment.

**Velocys, Inc.
Cumulative Budget to Actual for
MONTANA**

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 printed in the following publications:

- Business First – “Velocys lands \$400K research grant,” January 15, 2004
- Daily Reporter – “Local company’s business fueled by byproducts of landfills, coalmines,” January 15, 2004

Copies of the articles appear in Appendix III.

Experimental

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.

Experimental Description

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" OD housed within an outer tube of 3/4" OD. The length of the adsorbent bed is 6" inches, for a typical loading of 5-7 grams of adsorbent (based on 0.35-0.5g/mL density). A 50/50 mix of glycol and water heat exchange fluid flows through the annulus at 4 gallons/min. The fluid temperature can be varied from 0 °C to 80 °C, allowing testing with bed temperatures as high as 60 °C.

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 desorb the solutes between experiments.

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. The use of a back pressure regulator immediately downstream of the adsorbent bed allowed testing of adsorbents at pressures as high as 400 psig. After leaving the adsorption bed and before passing through the back pressure regulator to drop the pressure to near-ambient, 1 liter of argon was added to the outlet mixture to minimize the delay time between the analyzers and the bed exit (this represents a 50% dilution of the inlet gas flow). The outlet gases are then 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 CH₄/CO/CO₂ analyzer. Although not shown explicitly in Figure 2, the flow exiting the flowmeter in the sample analysis line is split to feed the nitrogen and CH₄/CO₂/CO analyzers in parallel.

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 procedure for running each experiment was as follows:

- 1) Grind adsorbent particles with mortar and pestle or small ball mill.
- 2) Sieve the particles to recover the 212-425 micron particle size fraction.
- 3) Load the test apparatus with a known weight of undried 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 (0, 100, 200, 300, or 400 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) Turn on the downstream of bed argon purge (1 SLPM).
- 10) 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.
- 11) Simultaneously start the feed to the adsorbent bed and stop the purge gas (argon) flow at time t_0 by opening the valve solenoid-1 and closing solenoid-2.
- 12) Record the measured outlet flow rates and compositions as a function of time via LabView program.
- 13) After steady-state is established, stop test by closing solenoid-1 and opening solenoid-2 (flow purge gas over the bed to remove the adsorbed solutes).

Once the testing is complete, the data can be recalled at any given time interval, but 0.5 second increments were used for the results reported here. 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 seconds at 100 psig) and the delay between the adsorbent bed exit and the analyzers (typically 1-3 seconds) were taken into account when calculating breakthrough time and capacity.

Adsorbents tested included three types of carbon and three types of zeolites. Adsorbent capacity was evaluated for all adsorbents at pressures of 2 psig and 100 psig and temperatures of 6, 23, 40, and 60 °C for 50/50 (v/v) and 90/10 (v/v) feed mixtures of methane and nitrogen. This was done so that for a given pressure and gas composition the differential capacity for methane between any two temperatures could be compared to the differential capacity for nitrogen between those same two temperatures. In addition, one of the most promising adsorbents (Calgon carbon) was tested for the above composition and bed temperature combinations at 200, 300, and 400 psig. Extra tests on the Barnaby-Sutcliffe carbon were also included using 10/90 (v/v) methane/nitrogen mixtures.

Because an improved experimental technique for measuring capacity (adding argon to the outlet flow to reduce the time required for the outlet flow to reach the analyzers) was developed, the PICA carbon capacity data collection reported in the previous quarterly report was repeated and revised results are reported. These data are thought to be more accurate than those previously reported for the PICA carbon.

Method for calculating capacity

In order to calculate the capacity of each adsorbent for methane and nitrogen, three types of responses were measured in real time and recorded every 0.5 seconds: the mass flow meter reading for total outlet flow, the mole fraction methane in the outlet, and the mole fraction nitrogen in the outlet (see Figure 3). The time at which the feed to the adsorbent bed was switched by solenoid valve from argon to the feed mixture was also recorded to the nearest 0.5 seconds. The adsorbent capacity was calculated for each component i (CH_4 or N_2) as in Equation 1:

$$\text{capacity} = \frac{n_{i, \text{adsorbed}} \cdot MW_i}{\text{grams adsorbent}} \quad (1)$$

where $n_{i, \text{adsorbed}}$ is the moles of component i adsorbed and MW_i is the corresponding molecular weight. The moles adsorbed of each component i was calculated by mass balance: moles adsorbed equals the cumulative number of moles entering the adsorbent bed ($n_{i, \text{in}}$) less the moles exiting the adsorbent bed ($n_{i, \text{out}}$) less the moles held up in the void space of the adsorbent bed ($n_{i, \text{bed}}$) as shown in Equation 2. Note that the cumulative moles in and the cumulative moles out do not include the gas flowing during the initial dead time (during which time argon is being purged from the inlet line and replaced with the feed mixture).

$$n_{i, \text{adsorbed}} = n_{i, \text{in}} - n_{i, \text{out}} - n_{i, \text{bed}} \quad (2)$$

Given the void volume of the adsorbent bed ($V_{\text{bed void}}$), the mole fraction of component in the inlet stream (y_i), and the bed temperature (T_{bed}) and pressure (P_{bed}), the moles held up in the adsorbent bed is easily calculated from the ideal gas law (Equation 3).

$$n_{i, \text{bed}} = \frac{P_{\text{bed}} \cdot y_i \cdot V_{\text{bed void}}}{R_{\text{gas, universal}} \cdot T_{\text{bed}}} \quad (3)$$

The cumulative moles entering the adsorbent bed is found as shown in Equation 4 below

$$n_{i, \text{in}} = \sum_{j=1}^n \text{SLPM } i \text{ in }_j \cdot \left(\frac{1 \text{ min}}{60 \text{ sec}} \right) \cdot \left(\frac{1 \text{ mol } i / \text{min}}{22.4 \text{ SLPM } i} \right) \cdot \Delta t_j \quad (4)$$

where “SLPM i in $_j$ ” is the flow rate of component i (CH₄ or N₂) in standard liters per minute (standard conditions being 0 °C and 1 atm) at the bed entrance at time j , and Δt_j is the time increment at time j in seconds. The cumulative moles leaving the adsorbent bed is found as shown in Equation 5 below:

$$n_{i, out} = \sum_{j=1}^n SLPM_{out_j} \cdot \left(\frac{1 \text{ min}}{60 \text{ sec}} \right) \cdot \left(\frac{1 \text{ mol / min}}{22.4 \text{ SLPM}} \right) \cdot y_{i,j} \cdot \Delta t_j \quad (5)$$

where “SLPM out $_j$ ” is the total flow rate out of the bed in standard liters per minute (standard conditions being 0 °C and 1 atm) at the bed exit at time j , y_{ij} is the mole fraction of component i at the bed exit at time j , and Δt_j is the time increment at time j in seconds. Note that since mole fractions were not measured at the bed exit, but further downstream at the analyzer after addition of additional Ar, the composition at the bed exit was assumed to be offset in time from the composition at the analyzer by the time required for the gas to travel between the two. The reading of the mass flow meter for the total outlet flow was offset from the actual total outlet flow by a factor which showed a linear dependence on gas composition as shown below in Equation 6.

$$F_{total, reading} = F_{Ar} \cdot K_{Ar} + F_{N_2} \cdot K_{N_2} + F_{CH_4} \cdot K_{CH_4} \quad (6)$$

In Equation 6, F_i represents the true flow rate in SLPM at the mass flow meter for each component i and the K_i values are correction factors determined from calibration with known mixtures of Ar, CH₄, and N₂ ($K_{Ar} = 0.964$, $K_{CH_4} = 1.889$, and $K_{N_2} = 1.431$). If $(F_{total, actual} - F_{N_2} - F_{CH_4})$ is substituted for F_{Ar} in Equation 6 and the equation re-arranged, the expression below (Equation 7) is obtained for actual total outlet flow rate.

$$F_{total, actual} = \frac{1}{K_{Ar}} \cdot [F_{total, reading} + F_{N_2} \cdot (K_{Ar} - K_{N_2}) + F_{CH_4} \cdot (K_{Ar} - K_{CH_4})] \quad (7)$$

Using the above equation, the actual total flow rate was iteratively calculated from the mass flow meter reading and the known composition of the gas at any given time. Iteration was necessary since only the mole fraction and not the flow rate of each component was known. The mass flow meter reading gave a good first guess for the iteration, which converged to give an actual flow rate after 2 iterations. The argon flow rate exiting the bed was calculated as the total argon flow rate $(F_{total, actual} - F_{N_2} - F_{CH_4})$ corresponding to the iterative solution to Equation 7 less the 1 SLPM downstream of bed purge argon flow.

It should be noted that the composition of the gas was measured at the gas analyzers, so the composition at the mass flow meter was assumed to be offset in time from the composition at the analyzer by the time required for the gas to travel between the two. In addition, a 1.2 second intrinsic methane analyzer delay was assumed as this gave a good match between the outlet flow readings and the methane analyzer readings under a wide variety of conditions. It was assumed that once the outlet composition reached an asymptotic value (at long run times beyond the point of breakthrough) that the outlet

molar flow rates were equivalent to the inlet molar flow rates. The reading from the continuous nitrogen analyzer consistently showed a sharp increase at the time which nitrogen began to be present in the outlet stream being analyzed. This sharp increase, or spike, was used to identify the beginning of the nitrogen peak (or N₂ peak start time, see Figure 3). Since the analyzer showed a complex dependency on time-on-stream as well as on methane and argon concentration, Equation 8 was used to simulate the nitrogen evolution step-function curve at the analyzer.

$$SLPM_{N_2} = \frac{\max SLPM_{N_2}}{1 + \exp\left[-\frac{(t - \tau_1)}{\tau_2}\right]} \quad (8)$$

where “max SLPM_{N₂}” is the asymptotic N₂ flow rate (based on inlet flows), t is the time in seconds, and τ_1 and τ_2 are fitting parameters which are adjusted to match the N₂ peak start time indicated by the N₂ analyzer and the calculated actual outlet total flow and argon flow as a function of time. The physical sense of τ_1 and τ_2 can be understood as follows: τ_1 is the average of the peak start time (detected by N₂ analyzer) and the peak duration time (in seconds), and τ_2 is the peak duration time in seconds divided by 8.8. Since the adsorbent bed was flushed with Ar before starting the flow of CH₄ and N₂ at the inlet, Ar gas was flushed out the exit of the bed during the time in which CH₄ and N₂ were adsorbed. The N₂ peak duration time was estimated via the response seen in the measured outlet flow (which is composition sensitive), adjusting the estimate until the calculated Ar outlet flow curve and calculated actual total outlet flow curves were smooth and continuous during the transition in composition of the outlet flow (see Figure 4). In a few cases, where the N₂ peak was obscured by the CH₄ peak, the N₂ peak duration time for the 90/10 CH₄/N₂ inlet mixture was assumed to be the same as for the 50/50 inlet mixture at the same conditions of temperature and pressure (see Figure 5). Although this method of nitrogen evolution estimation introduces some additional error into the nitrogen capacity measurement, the effect seems to be minor (less than 10%) in most cases.

Figure 3. Outlet flow rate reading from mass flow meter (left axis) and nitrogen and methane analyzer readings (right axis, before calibration correction) for adsorption capacity tests on Calgon carbon adsorbent using an equimolar feed mixture at 60 °C and 100 psig. Dead time was 7 seconds.

Figure 4. Outlet flow rate reading from mass flow meter and corrected total outlet flow (left axis) and argon, nitrogen, and methane flows at the sorbent bed exit (right axis) for adsorption capacity tests on Calgon carbon adsorbent while feeding 0.5 SLPM CH₄ and 0.5 SLPM N₂ at 60 °C and 100 psig. Dead time was 7 seconds.

Figure 5. Outlet flow rate reading from mass flow meter and corrected total outlet flow (left axis) and argon, nitrogen, and methane flows at the sorbent bed exit (right axis) for adsorption capacity tests on Calgon carbon adsorbent while feeding 0.9 SLPM CH₄ and 0.1 SLPM N₂ at 60 °C and 100 psig. Dead time was 7 seconds.

Task 2.1 Conceptual System Process Design

Task Objective

The goals of the Conceptual System Process Design, or simply the system study used in this text, are as follows:

- Define the critical unit operations, including order
- Mass and energy balance of the required unit operations
- Capacity (duty) and performance assumptions of each identified unit operation
- Temperature, pressure, flow rate, and composition of each process stream
- Summary metrics of product recovery and thermal efficiency

System Design Basis

To provide a basis for the system study, several variables were fixed and conventions adopted.

- The methane upgrading system was sized for 3 million standard cubic feet per day (MMSCFD) of sub-quality natural gas entering from a gob gas well or wells
- Composition of the gas from the well is: 70% CH₄, 4% O₂, 22% N₂, 4% CO₂ and saturated with water at ambient conditions
- Composition required for the pipeline: 96% CH₄, <4% N₂ or CO₂, 10 ppm O₂ and dry to -40°C at 600 psi
- Inlet temperature and pressure from the well: 20°C and 1 psig
- Outlet temperature and pressure to pipeline: <200°C and 600 psig

The results and implications are discussed in the Results and Discussion section.

Results and Discussion

Task 1.2 Adsorbent Validation

Typical analyzer and mass flow meter reading curves are shown in Figure 3. Figures 4 and 5 depict outlet flow curves produced from typical tests at 100 psig with mixtures of 50/50 and 90/10 (v/v) methane/nitrogen, respectively. The results of the adsorbent capacity screening tests are shown in Tables 1-5. Tables 1 and 2 summarize the measured *carbon* adsorbent capacities for the 2 psig and 100 psig tests, respectively. Table 3 shows the measured Calgon carbon adsorbent capacities for the 200, 300, and 400 psig tests. Tables 4 and 5 summarize the measured *zeolite* adsorbent capacities for the 2 psig and 100 psig tests, respectively. The zeolite adsorbents were obtained from Alpha Aesar and xxxxx. These capacities can then be used to determine differential capacities between any two temperature conditions for a given inlet composition and pressure (the differential capacity for a given component is simply the difference between the two measured capacities for that component at the low and high temperature).

It is desirable to have a high of the differential capacities for methane and a low differential capacity for nitrogen over a given temperature range in order to effect separation by thermal swing adsorption. In general, the carbon adsorbents had much higher differential capacities than the zeolite adsorbents over the range of conditions tested. The 2 psig pressure capacities were always lower than the corresponding 100 psig capacities, so the best adsorbent for a 90/10 mixture over the interval of 40-60 °C was identified from the data at 100 psig. This adsorbent (Calgon) was further tested at 200, 300, and 400 psig, but surprisingly, performance at these higher pressures showed no significant increase in differential capacity as compared to the 100 psig performance.

It is also noted that the values of adsorbent capacity reported here for methane and nitrogen on the PICA carbon are somewhat different than those reported previously. The new data were taken after making improvements in the testing system. These improvements to the system have yielded both higher quality data and a self consistent comparison between all six adsorbents.

Table 1. Carbon sorbent capacities measured over a range of temperature and feed mixture compositions at near ambient pressure.

Carbon sorbents- 2 psig			Barnaby-Sutcliffe		Calgon		PICA	
Temp (C)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	100	900	6.5	10.1	-	-	-	-
6	500	500	19.7	7.7	16.4	6.4	18.2	7.6
6	900	100	26.7	2.5	23.6	1.9	24.6	2.1
23	100	900	3.8	5.7	-	-	-	-
23	500	500	12.3	4.8	11.4	4.2	13.3	6.3
23	900	100	18.2	1.4	16.1	1.3	16.9	1.6
40	100	900	2.3	3.2	-	-	-	-
40	500	500	9.4	2.8	7.8	4.3	8.4	5.0
40	900	100	12.3	0.9	9.5	1.0	10.9	1.3
60	100	900	1.7	4.3	-	-	-	-
60	500	500	5.1	2.4	4.8	2.9	4.9	2.9
60	900	100	8.3	0.5	7.1	0.8	5.7	0.9

Table 2. Carbon adsorbent capacities measured at 100 psig

Carbon sorbents- 100 psig			Barnaby-Sutcliffe		Calgon		PICA	
Temp (C)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	100	900	16.5	40.7	-	-	-	-
6	500	500	55.5	27.1	44.4	22.5	54.9	28.6
6	900	100	75.7	6.1	63.0	5.0	75.0	5.9
23	100	900	12.4	32.1	-	-	-	-
23	500	500	44.2	25.6	36.0	18.7	40.0	18.9
23	900	100	57.8	5.1	54.6	4.1	59.6	4.3
40	100	900	8.6	24.9	-	-	-	-
40	500	500	36.9	22.8	31.7	17.6	28.9	13.3
40	900	100	48.1	4.4	41.6	3.5	42.9	2.6
60	100	900	7.5	22.2	-	-	-	-
60	500	500	28.0	18.4	23.4	10.7	25.3	11.1
60	900	100	39.6	3.8	31.8	2.5	35.3	2.6

Table 3. Measured Calgon carbon sorbent capacities as a function of temperature and mixture composition for 200, 300, and 400 psig bed pressures.

Calgon carbon- high P			200 psig		300 psig		400 psig	
Temp (C)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	500	500	52.1	29.8	66.5	40.0	76.1	45.1
6	900	100	66.2	6.3	91.4	8.5	112.7	10.2
23	500	500	41.8	23.8	51.2	34.2	65.5	39.5
23	900	100	63.1	5.4	81.3	7.5	95.2	8.4
40	500	500	35.3	22.0	43.2	26.7	50.5	31.7
40	900	100	51.5	4.6	70.2	6.3	87.5	8.3
60	500	500	33.2	18.4	39.4	25.8	54.6	32.9
60	900	100	45.4	3.8	63.3	5.3	84.6	7.4

Table 4. Zeolite adsorbent capacities measured over a range of temperature and feed mixture compositions at near ambient pressure.

Zeolites, 2 psig			Z-10-02		Z-10-06		Alpha Aesar	
Temp (C)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	500	500	5.5	3.3	5.7	5.5	4.7	4.2
6	900	100	7.5	1.2	8.2	1.4	6.9	0.9
23	500	500			3.6	2.6	3.1	2.2
23	900	100			6.4	0.8	4.7	0.4
40	500	500	1.8	1.4	3.2	2.0	2.4	1.8
40	900	100	2.1	1.3	4.1	1.0	2.5	0.3
60	500	500			1.5	1.6	1.0	0.9
60	900	100			2.5	0.6	1.2	0.2

Table 5. Zeolite adsorbent capacities measured at 100 psig

Zeolites, 100 psig			Z-10-02		Z-10-06		Alpha Aesar	
Temp (C)	CH4 flow (sccm)	N2 Flow (sccm)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)	CH4 Capacity (mg/g)	N2 Capacity (mg/g)
6	500	500	24.5	14.2	24.7	14.7	21.7	13.7
6	900	100	36.0	4.4	39.1	4.5	34.0	3.4
23	500	500			18.6	13.9	16.8	9.2
23	900	100			28.0	3.2	28.2	2.4
40	500	500	15.5	9.3	15.8	8.9	12.4	7.1
40	900	100	23.7	2.1	24.3	2.1	20.9	1.7
60	500	500			13.4	8.7	-	-
60	900	100			22.5	2.0	-	-

Task 2.1 System Design

Methane Upgrading System

The system study evaluated the complete process for upgrading coal-bed methane to pipeline quality. This process, as shown in Figure 6, consists of six steps: process compression, dehydration, nitrogen rejection, oxygen removal, carbon dioxide rejection and sales compression. Below is a simplified diagram showing the basic processing steps.

Figure 6 – Methane upgrading process system configuration

The complete process was modeled in detail using ChemCAD, a process simulation software package. The resulting process flow diagram and stream table can be seen in Appendices I and II. The case displayed assumes that the Velocys Technology NRU can achieve 90% recovery, the target recovery and system design point.

The requirements and equipment needed to perform the major processing step are discussed. Background information for the technology and economics are reported from an EPA Coalbed Methane Outreach Program study titled, Technical and Economic Assessment of Potential to Upgrade Gob Gas to Pipeline Quality, and published in 1997.

Compression

The methane upgrading system requires two separate gas compression operations. To enter the process the gob gas stream must be pressurized from 1 to approximately 120 psig. Then after the final upgrading processing step (CO₂ removal), the product gas must again be compressed to 600 psig to enter the sales natural gas pipeline.

The feed compressor requires two stages and approximately 250 horsepower to compress the entire 3 MMSCFD of sub-quality gas. The estimated cost of this unit, including inter and after coolers, vapor-liquid separators and associated auxiliary equipment is \$477,000.

Sales compression is less costly (estimated at \$190,000) for two reasons. First, only one stage is required to raise the pressure of a gas stream from 100 psig (after a 20 psi loss through the upgrading system) to 600 psig. Second, the quantity of gas remaining after the processing steps is less than 2 MMSCFD. The large volume reduction is due to the removal of sub-quality components, such as nitrogen and carbon dioxide, and the loss of some methane.

Dehydration

Compression will reduce the concentration of water vapor to the dew point (saturation) at the inlet to the removal stage; for example the water vapor dew point at 600 psig is 78°C (172°F) and 0.47 mole percent. Therefore addition dehydration is needed to meet the pipeline specification of -40°C dew point (0.00039 mole percent water vapor). Typically molecular sieves are used to remove water vapor from natural gas processes and represent a commercial basis for this unit operation. The dehydration subsystem capital cost is estimated to be \$40,000 for a 3 MMSCFD plant; this is consistent with the EPA report.

Nitrogen Recovery Subsystem

As the NRU is the focus of the project, the cost target and macro processing conditions are exclusively discussed in this section. Salient details gleaned from the system study and computational modeling are described in a dedicated section below.

The price target for a 3 MMSCFD Velocys Technology NRU is \$1.35 million, which is a 20 percent capital cost reduction compared to conventional technology. The benchmark pricing for a pressure swing adsorption (PSA) system with a similar capacity is from the EPA report.

The Ultra-Fast TSA system will cycle between 40 and 60°C every two seconds, one second per phase, and achieve a methane recovery rate of 90 percent. The tail gas, containing the remaining 10 percent of the methane will be used to provide the energy needed to swing the adsorber temperature. The operating pressure will be 120 psig and the predicted system pressure drop will be approximately 10 psig.

Catalytic Oxygen Removal

A significant fraction of the oxygen may be removed with the nitrogen in the NRU. However, a separate Oxygen Removal unit operation is included in this preliminary evaluation. Catalytic combustion of methane and oxygen is expected to reduce the oxygen concentration below the specified concentration of 10 parts per million (ppm) for pipeline natural gas. The scaled subsystem capital cost for this unit operation is estimated to be \$280,000 for approximately 2 MMSCFD gas in the product stream after the NRU.

Carbon Dioxide Removal

An amine carbon dioxide (CO₂) removal system is typically used for natural gas and petrochemical processing. This represents a commercial basis for this unit operation. The scaled subsystem capital cost for this unit operation is estimated to be \$150,000 for

the remaining 2 MMSCFD of product gas. Membranes or Engelhard’s Molecular Gate (a specialized PSA adsorbent) offer alternative techniques but the installed costs are comparable to amine systems.

Cost Comparison

Based upon the Velocys Technology NRU achieving the operational and cost targets, the resulting methane upgrading system should have a distinct cost advantage. The graph in Figure 7 shows the results of a preliminary system cost study and compares the results with a case from the EPA study (benchmark). Note that the costing data will be further refined later in the project and estimates may change.

Figure 7 – Preliminary system cost comparison (3 MMSCFD basis)

Nitrogen Rejection Unit

This section of the system study focuses on the final stated objective: summary metrics of product recovery and thermal efficiency. To determine these key parameters a mathematical model was developed to simulate a multi-stage nitrogen recovery unit (NRU). A series of runs were performed on the model with the following objectives:

- To determine key parameters governing energy requirements for a Nitrogen Removal Unit (NRU).
- To design system to deliver required energy to NRU.

Figure 8 shows the schematic of the model NRU system. The theoretical NRU has channels housing adsorbent material adjacent to heat exchange channels. The heat exchange channels are used to swing the bed temperature between the adsorbing and

desorbing temperature state. The feed gas enters the low temperature adsorbent section of the NRU to preferentially adsorb methane. A nitrogen rich exhaust stream, labeled ‘tail gas’, is rejected out of the unit prior to breakthrough of the product methane. After the adsorber unit is filled to capacity with methane, the device is heated to desorb methane. In order to flush removed methane out of the box, a small quantity of “flush gas” may be flowed, but this may not be necessary. The methane released from the desorption cycle may become the feed for the next stage or collected as product if sufficient purity is attained.

Figure 8 – Nitrogen Rejection Unit schematic

The inputs to the computational NRU model are:

- Channel dimensions
- Adsorbent Characteristics
- Inlet Feed gas composition and outlet methane flow rate
- Adsorption/desorption temperature and cycle time
- Construction material of box

By varying the following inputs, two potential NRU design concepts were developed. The first, called ‘early entry,’ requires more energy to swing the temperature of the adsorbent bed but is expected to be a more straight-forward development effort. The second, which uses an engineered form of the adsorbent material, is expected to have a longer development effort, but will result in improved methane recovery and reduced energy consumption. The specifics of each concept are presented in Table 6.

Table 6. NRU process performance targets and anticipated performance

	<u>Early Entry</u>	<u>Engineered Form</u>
Material of Construction	Stainless Steel	Porous Carbon Engineered
Adsorbent Form	Powdered	Form/Stainless Steel
		Composite
Cycle Time	1 to 5 seconds	1 to 3 seconds
Energy Requirement	1.5 MW	408 kW
Methane Recovery	80%	95%

Heating and Cooling System for NRU

Integral pieces of the NRU are the heating and cooling systems that permit the rapid temperature swings. A schematic of these systems is shown below in Figure 9.

Figure 9 – NRU Heating and Cooling Systems

The system is fueled by methane in the tail gas, which is combusted with air to provide heat to desorb the bed. An efficiency of 70% was assumed for heat transfer from combusted gas to the nitrogen rejection unit. Achieving this energy efficiency may require the use of efficient microchannel exchangers. The heat from the combusted gases is transferred to a circulating fluid which flows through the NRU system to provide heat to the desorption cycle.

Other sources of heat, such as inter-stage and/or after coolers on the compression equipment, may also be used to affect the thermal swing. If these other sources can be tapped, then a further reduction in the amount of tail gas methane required for the desorption cycle is possible.

For the adsorption cycle, heat is removed from the NRU system by a cooling circuit, as shown in Figure 4. A cooling fluid removes heat from the NRU system. In a closed-loop process, heat is rejected to ambient from the cooling fluid prior to returning into the adsorber unit.

Conclusions

Measured adsorption capacity and differential capacity between 40 and 60 C was highest on microporous carbon. Both the Calgon AX-21 carbon and the Barnaby-Sutcliffe carbon gave similar performance at 100 psig. Surprisingly, the performance at 100 psig was better than either low pressure (2 psig) or higher pressure (>200 psig) for the Calgon carbon. An operating pressure of 100 psig was selected for the system study

A system design was completed for upgrading sub-quality methane to natural gas pipeline quality. The Velocys NRU is anticipated to generate at least 96% methane purity and recover at least 80% of the methane. A next generation design is also being investigated to increase the methane recovery to 95%.

Plans for the third quarter of FY04 are as follows:

- Complete the conceptual process and component design for the Velocys NRU (Task 2.1)
- Complete the cost and feasibility assessment (Task 3)
- Initiate planning for the bench-scale demonstration (Task 4)

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

Process Flow Diagram for Methane Upgrading System

Appendix II

Stream Composition for Appendix I

ChemCAD/Montana/Metric PFD 3.0 feed, dated 23 March 2004

Stream No.	1	11	12	13	14	15	21	22	31	32	41	51	52	61	62	63
Name	Raw Gas Feed															
-- Overall --																
Molar flow kmol/h	158.5	158.5	158.5	157.7098	0	0.7903	155.5002	2.2095	103.9102	51.59	103.9099	99.4154	4.4944	99.4154	99.4154	0
Mass flow kg/h	3197.274	3197.274	3197.274	3183.038	0	14.2365	3143.233	39.8045	1798.11	1345.123	1798.111	1600.311	197.7998	1600.311	1600.311	0
Temp C	20	617.3591	48.8889	48.8889	0	48.8889	48.8889	48.8889	48.8889	48.8889	57.2449	57.2449	57.2449	238.526	45	0
Pres psia	1	125	123	123	0	123	123	123	113	113	113	113	113	620	618	0
Vapor mole fraction	1	1	0.995	1	0	0	1	0	1	1	1	1	1	1	1	0
Enth kW	-2988.2	-1782	-2958.4	-2896	0	-62.391	-2747.9	-174.44	-2528.7	-218.98	-2528.6	-2038.5	-490.09	-1831.6	-2065.3	0
Average mol wt	20.1721	20.1721	20.1721	20.1829	0	18.015	20.2137	18.015	17.3045	26.0733	17.3045	16.0972	44.01	16.0972	16.0972	0
Actual vol MMt3/day	47.4779	1.1572	0.4186	0.4186	0	0	0.4131	0	0.2996	0.1501	0.3077	0.2945	0.0131	0.0843	0.0496	0
Std liq liter/hr	7548.206	7548.206	7548.206	7533.968	0	14.2388	7494.157	39.8109	5548.272	1945.885	5547.422	5308.206	239.216	5308.206	5308.206	0
Std vap 0 C MMscfd	3.011	3.011	3.011	2.996	0	0.015	2.954	0.042	1.974	0.98	1.9739	1.8886	0.0854	1.8886	1.8886	0
Stream No.	1	11	12	13	14	15	21	22	31	32	41	51	52	61	62	63
Name	Raw Gas Feed															
Temp C	20	617.3591	48.8889	48.8889	617.3591	48.8889	48.8889	48.8889	48.8889	48.8889	57.2449	57.2449	57.2449	238.526	45	238.526
Pres psia	1	125	123	123	125	123	123	123	113	113	113	113	113	620	618	620
Enth kW	-2988.2	-1782	-2958.4	-2896	0	-62.391	-2747.9	-174.44	-2528.7	-218.98	-2528.6	-2038.5	-490.09	-1831.6	-2065.3	0
Vapor mole fraction	1	1	0.99501	1	0	0	1	0	1	1	1	1	1	1	1	0
Total kmol/h	158.5	158.5	158.5	157.7098	0	0.7903	155.5002	2.2095	103.9102	51.59	103.9099	99.4154	4.4944	99.4154	99.4154	0
Flowrates in kmol/h																
Methane	110	110	110	110	0	0	110	0	99	11	98.9588	98.9588	0	98.9588	98.9588	0
Ethane	0	0	0	0	0	0	0	0	0	0	0.0007	0.0007	0	0.0007	0.0007	0
Propane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-Butane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	3	3	3	2.2097	0	0.7903	0.0002	2.2095	0.0002	0	0.0806	0.0806	0	0.0806	0.0806	0
Nitrogen	33	33	33	33	0	0	33	0	0.33	32.67	0.33	0.33	0	0.33	0.33	0
Oxygen	8	8	8	8	0	0	8	0	0.08	7.92	0	0	0	0	0	0
Carbon Dioxide	4.5	4.5	4.5	4.5	0	0	4.5	0	4.5	0	4.5398	0.0454	4.4944	0.0454	0.0454	0
Stream No.	1	11	12	13	14	15	21	22	31	32	41	51	52	61	62	63
Name	Raw Gas Feed															
Temp C	20	617.3591	48.8889	48.8889	617.3591	48.8889	48.8889	48.8889	48.8889	48.8889	57.2449	57.2449	57.2449	238.526	45	238.526
Pres psia	1	125	123	123	125	123	123	123	113	113	113	113	113	620	618	620
Enth kW	-2988.2	-1782	-2958.4	-2896	0	-62.391	-2747.9	-174.44	-2528.7	-218.98	-2528.6	-2038.5	-490.09	-1831.6	-2065.3	0
Vapor mole fraction	1	1	0.99501	1	0	0	1	0	1	1	1	1	1	1	1	0
Total kmol/h	158.5	158.5	158.5	157.7098	0	0.7903	155.5002	2.2095	103.9102	51.59	103.9099	99.4154	4.4944	99.4154	99.4154	0
Component mole %																
Methane	69.40063	69.40063	69.40063	69.74838	0	0	70.73944	0	95.27455	21.32196	95.23521	99.54066	0	99.54066	99.54066	0
Ethane	0	0	0	0	0	0	0	0	0	0	0.00068	0.00069	0	0.00069	0.00069	0
Propane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-Butane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	1.892745	1.892745	1.892745	1.401144	0	100	0.000142	100	0.000213	0	0.077538	0.081043	0	0.081043	0.081043	0
Nitrogen	20.82019	20.82019	20.82019	20.92452	0	0	21.22183	0	0.317581	63.32623	0.317582	0.33194	0	0.33194	0.33194	0
Oxygen	5.047318	5.047318	5.047318	5.072609	0	0	5.144687	0	0.076989	15.35181	0	0	0	0	0	0
Carbon Dioxide	2.839117	2.839117	2.839117	2.853343	0	0	2.893886	0	4.330662	0	4.369004	0.045665	100	0.045665	0.045665	0

THE DAILY REPORTER

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Local company's business fueled by byproduct of landfills, coal mines

By BOB PASCHEN
Daily Reporter Staff Writer

Imagine using landfills for energy, or dirty coal shaft methane as a source of natural gas. These and other new energy avenues are just what Central Ohio-based Velocys Inc. is pursuing, and with a recent \$400,000 grant from the Department of Energy, the company just came one step closer to making their ideas a reality.

Throughout the U.S. are numerous sources of natural gas, Velocys spokesman Jeff McDaniel said. Often the gas is mixed with other chemicals, though, and the cost or energy-input required to extract the pure natural gas from the impurities renders much of the domestic energy source unusable.

Velocys thinks it has technology that could both tap previously unused gas fields and turn some pollutants into valuable sources of energy.

Looking from afar like enormous piles of steaming spaghetti, heaps of rotting trash in landfills produce copious amounts of methane, and this gas can create problems.

According to the Environmental Protection Agency's Web site:

"Most of the waste we generate ends up in landfills where it decomposes and produces landfill gas.

Landfills often use pipes to trap emitted methane gas. This fuel eventually can be "put into the power grid" to power homes. Velocys is trying to develop technology that would simplify the purification process, making it cheaper and efficient.

Landfill gas, if uncontrolled, can contribute to local smog and present health and safety hazards. Additionally, landfill gas is approximately 50 percent methane, a potent greenhouse gas that contributes to global climate change."

To mitigate the environmental impact, the EPA stipulates that all landfills now must have inter-heap piping to trap methane.

John Remy, director of communications for the Solid Waste Authority of Central Ohio, said the Franklin County dump had a sub-structure of piping in place before any trash came in.

For years, the common practice nationwide was to simply burn the collected gas. Remy called it "flar-

ing off," which is what currently is done at the new county dump.

But, with advanced technology, scientists discovered ways to harness the trash gas and use it for energy generation.

A 2001 EPA study on a South Carolina landfill found that annual energy output from trapped gas would be equivalent to 155 railroad cars of coal or 73,000 barrels of oil.

Remy said the old county dump, which now sits below Phoenix Golf Course, near Interstate 71 south of Columbus, uses pipes to trap emitted gas. This fuel is then "put into the power grid and powers thousands of homes."

(See Byproduct, Page 3)

Byproduct

(Continued from Page 1)

But there is an elaborate system of purification that must first occur before the gas is pipeline-quality, McDaniel said. Velocys is trying to develop technology that would simplify the process, making it cheaper and efficient, and making the capture of landfill gas more prevalent nationwide.

And gas in coal mines is analogous to that found in landfills, McDaniel said.

"Typically, where you have coal you have methane," he said. "And methane is a main component in natural gas." The problem, again, though, is gas contamination.

"These coal gas streams tend to contain a lot of impurities and thus are not usable. If you could efficiently extract the gas, you could reduce methane emissions, which is a potent environmental pollutant, and then you could purify and use the natural gas."

At present, the common method for gas capture and purification is called "cryogenic separation," McDaniel said, noting that this low-temperature, cost-intensive process is energy-inefficient.

However, it is "kind of common" for coal companies to let shaft methane rise to the surface and emit it freely to the air, or burn it, emitting carbon dioxide into the atmosphere, McDaniel said.

Besides the environmental issues, he added, these companies are losing out on a potentially-lucrative power supply.

Scientists at Velocys, which is an independent spin-off of Battelle, developed technology by which coal shaft methane, as well as landfill gas, can be converted into usable fuel.

Pipeline-grade natural gas has less than four percent impurities, McDaniel said. To get fuel to that level, the purification process can be intense. Some low-grade natural gas can be used to run boilers or for other industrial operations, but to ship gas to other markets, the fuel must be high-grade.

Employing its patented microchannel process technology, Velocys can heat dirty gas and molecularly separate the unusable components from the pure fuel.

McDaniel noted that MPT not only can upgrade landfill and coal shaft gas extraction processes, but it should find a niche market in the 15 percent of domestic natural gas fields that have thus far been considered unable to be tapped. They were not tapped, he said, because the mostly nitrogen-suffused fuel was considered below quality.

Wayne Simmons, chief executive officer of Velocys, said that "solving the methane problem for coal mines and landfills would open economic avenues for upgrading or recovering methane from other sources, such as upgrading nitrogen contaminated, geological natural gas."

Company number crunchers have stated that when commercially-deployed, MPT-based-separation/purification systems "have the potential to reduce annual greenhouse gas emissions by 23.5 billion equivalent kilograms of carbon dioxide, and 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."

The \$400,000 Department of Energy grant will allow Velocys to make a testable prototype that could find a home at landfills and coal mines across the country.

Business First text:

Velocys lands \$400K research grant

Velocys Inc. of Plain City will use a \$400,000 grant from the U.S. Energy Department to develop devices to trap methane gas.

Velocys will use its proprietary technology to attempt to build machinery to trap methane gas from coal mines, landfills, natural gas fields and other industries. Methane gas is thought to contribute to global warming.

Velocys was founded by the Battelle Memorial Institute, a Columbus-based research institute, in 2001.