Laboratory-Sized PSA/VSA Instrument for Screening Adsorbents for CH4 Upgrading

J. Adolphs, Porotec GmbH, Hofheim/D
A. Venero, L&C Science, Hialeah, FL/USA

Introduction

The need to upgrade the quality of CH4 from diverse sources including coal and biomass gasification, hydraulic fracturing and coal-bed methane has increased in the last 10 years. Among the techniques available for cleaning CH4, PSA (Pressure Swing Adsorption) and VSA(Vacuum Swing Adsorption) offer many advantages among them simplicity and economy, especially for remote and small scale operations where other separation techniques are either too costly or impossible to apply.

The gas obtained for the different sources must be upgraded to pipeline quality gas which implies CO2 and N2 molar concentrations below 2.5% (1).

Traditionally zeolites and activated carbons had been the adsorbent of choice for CH4 upgrading but with the discovery of Molecular Gates (2) , metal organic frameworks(MOFs)(3,4)and covalent organic frameworks(COFs)(5), the number of possible adsorbents for CH4 upgrading has substantially increased and with it the need to test these materials under PSA process conditions.

For the purpose of screening adsorbents suitable for CH4 remediation, a fully automated dual bed PSA/VSA was designed and constructed that allows for small adsorbent beds and flexibility of experimental parameters of flow, pressure temperature and cycle times. The system's performance will be demonstrated by the separation of N2 and CO2 from a CH4 stream using a commercial 13-X zeolite adsorbent. The effects of pressure, temperature, cycle time, purge and vacuum on the separation efficiency will be also presented.

Experimental: Instrument and Adsorbent Media

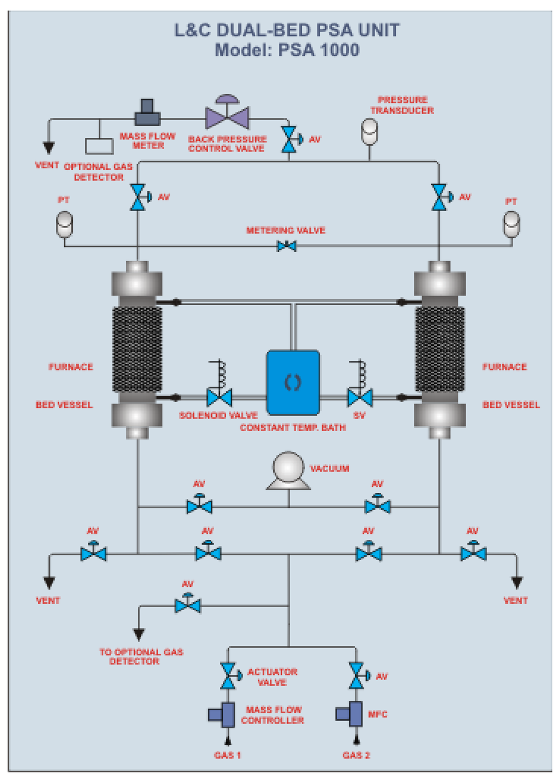

Figure 1. Schematic of the PSA System

The PSA/VSA system used in the breakthrough and cycling experiments was a dual-bed system (Model PSA-1000 from L & C Science, Hialeah, FL. USA). A description of the system is given in Figure 1.

The adsorbent used was a 13-X zeolite material from Sigma-Aldrich Chemicals. The zeolite particles were spherically shaped with diameters ranging from 1.4 to 2 mm (Tyler MESH sizes 8 to 12). The isotherms for this material with N2, CH4 and CO2 at 298 and 308 K and pressures up to 1300 kPa are shown in Figure 2.

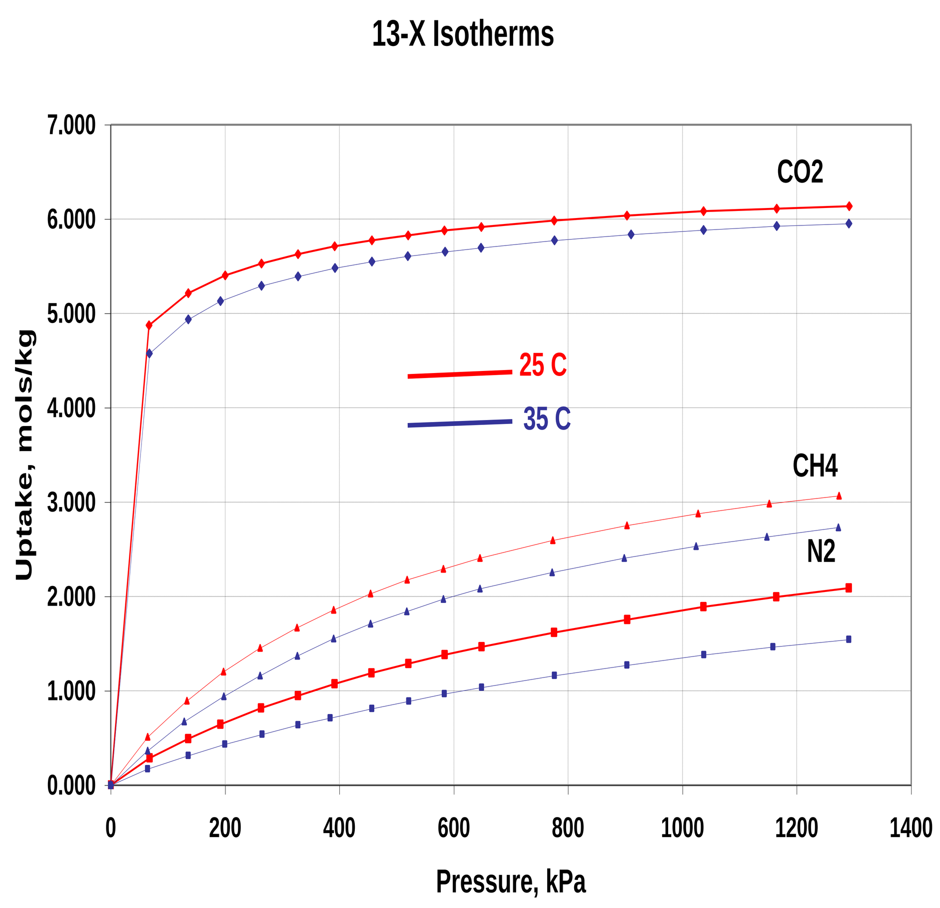

Figure 2. CH4, CO2 and N2 Isotherms for 13-X

The characteristics of the two adsorption beds are given in Table 1.

Bed Diameter, m	0.0211
Bed Active Length, m	0.718
Bed Density, kg/m^3	676
Adsorbent Volume, m^3	2.5x10^{-4}

Table 1. Adsorption Bed Properties

PSA Runs

The gas composition selected, 60% CH4, 20% CO2 and 20% N2, was the same used by Cavenati *et al*(1) in their PSA/VSA work . Six different runs were carried out with the same total flow rates for the feed (2SLM), adsorption pressure (500 kPa) , purge (0.1 SLM) but different cycle times , blow down sequence and two different temperatures: 298 K and 318 K. In one series of experiments the system was blow down to a pressure of 20 kPa right after the adsorption or feed step and in the other series the two beds were pressure equalized before one was blow down and the other pressurized. A representation of the two cycle configurations is given in Figure 3.

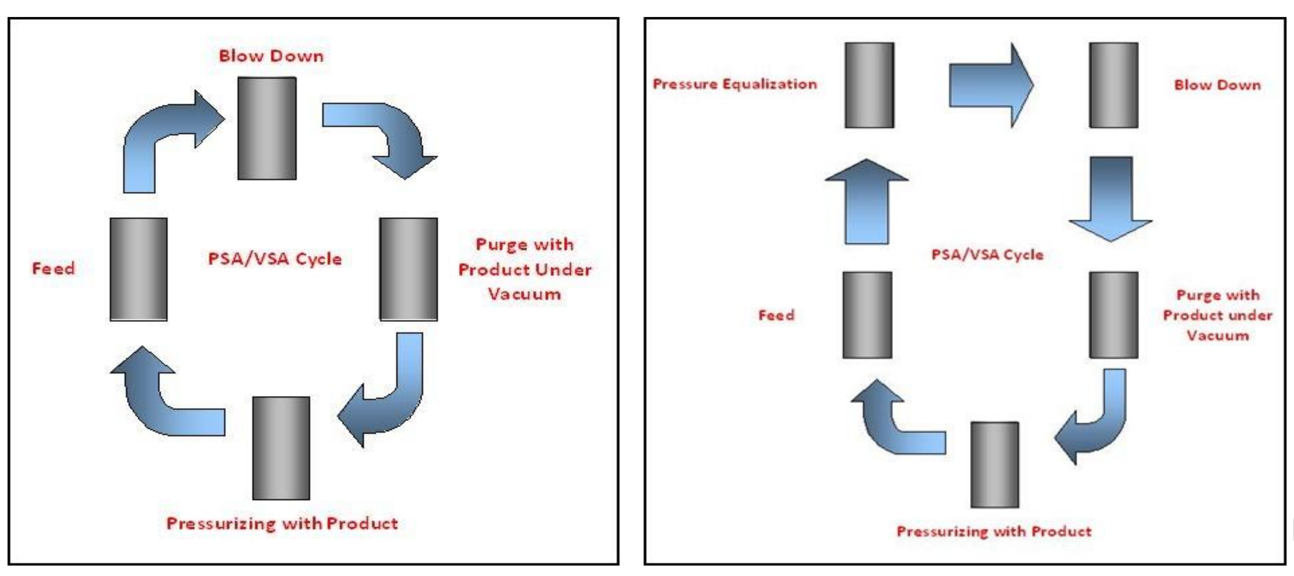

Figure 3. PSA Cycle

Results

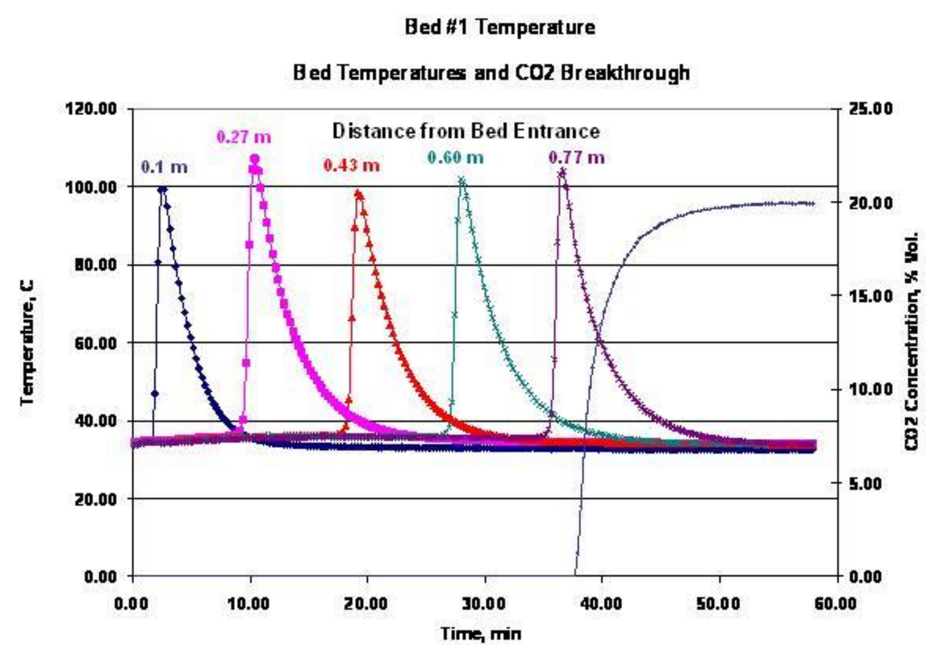

Figure 4. Breakthrough Curve for CO2 and Bed Temperatures

The first experiment was to determine the breakthrough for CO2 at 5 bars, 298 K and a concentration of 20% and 80% CH4. The total flow rate of the gas was 2 SLM. In Figure 3 the breakthrough experiment is shown(for CO2 only) together with the temperature rise in the zeolite bed.

In Figure 5 and 6 bed pressures and bed temperatures are shown for run 4 (The different runs are listed in Table 2).

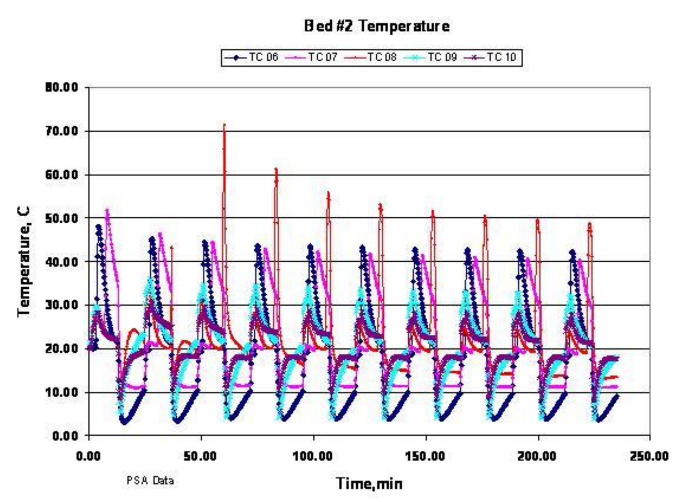

Figure 5. Temperature profile in Bed #2 for Run #4

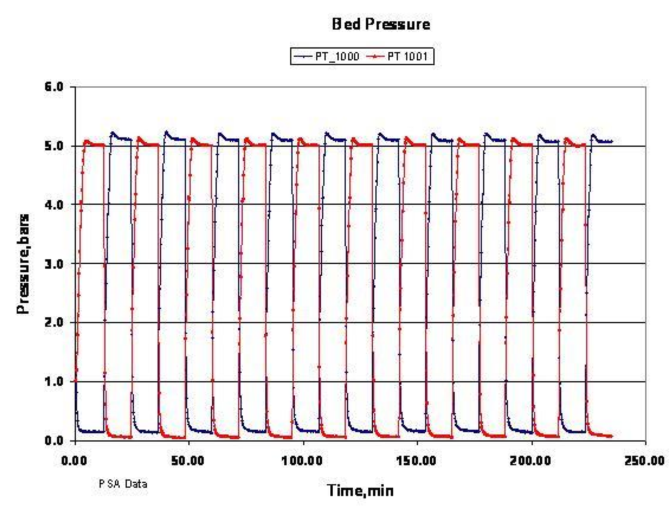

Figure 6. Pressure During Cycling for Run # 4

Run	Pressurization,s	Feed,s	Purge,s	Product,CO_2 %	CH4 Recovery,%	T, K
1	195	195	250	0.0	63.5	298
2	180	600	550	0.0	82.0	298
3	75*	300	250	01	82.9	298
4	75*	600	550	0.1	95.6	298
5	60*	300	250	0.2	88.2	318
6	60*	600	550	0.5	97.8	318

***Runs with Pressure Equalization Prior to Blow Down**

Table 2. Results of the PSA runs with zeolite 13-X at 500kPa and 2 SLM flow

Conclusions

From Table 2 one can conclude the following regarding the PSA process:

1. Increasing the feed time improves the bed utilization and CH4 recovery without impacting on the CO2 concentration in the product.

2. By pressure equalization prior to blow down and purge one can substantially increase the CH4 recovery without impacting on the CO2 concentration.

3. The best results in terms of CH4 recovery are obtained with longer feed times and pressure equalization.

4.Although the CO2 concentration in the product is very low, still the overall purity of the process gas is not much higher than 80% in all these runs because of the fast breakthrough of N2.

5.The lab-sized PSA system it is very well suited for the purpose of screening materials for CH4 upgrading and for optimization of the PSA/VSA process.

References

1. M.M. Foss," *Interstate Natural Gas-Quality, Specifications and Interchangeability*", Center for Energy Economics, The University of Texas, 2004.
2. S.M. Kuznicki, V.H. Bell, S. Nair, H.W. Hillhouse, R.M. Jacoubinas, C.M. Braunbarth, B.H. Toby and M.Tsapatsis, *Nature,412,720-724,2001*.
3. L.Bastin, P.S. Barcia, E.J. Hurtado, J.A.C. Silva, A.E. Rodrigues and B.Chen,*J.Phys.Chem.,C,112(5),1575-1581,2008.*
4. B.J. Alnemrat, L.Yu,I.Vasiliev, Q.Ren, X.Lu and S.Deng, *J.Colloid Interface Sci.,357(2),504-507,2011.*
5. J.L. Mendoza-Cortes,S.S. Han, H.Furukawa, O.M.Yaghi and W.A. Goddard, *J.Phys.Chem,A,114(40),10824-10833,2010.*