Technical Article

Laboratory Scale Assessment of Adsorbents for Gas Separation Applications

Adsorption is widely used to separate and purify gases. Process design and optimisation plays a crucial role in the practical implementation of this technology, but laboratory scale studies are required in order to initially assess the suitability of new materials for practical use. Preliminary analytical measurements can be made with pure gases; for example, N_2 adsorption measurements performed at 77 K for surface area determination are now a routine part of the porous material characterisation process. As a next step towards determining the capability of a material for a given separation, however, adsorption measurements with mixtures are necessary. The difficulty is that equilibrium multicomponent gas and vapour adsorption measurements are challenging and time-consuming (Broom and Thomas, 2013). A more efficient alternative is the use of chromatographic techniques, including the measurement of breakthrough curves, which we will focus on in this article.

In a breakthrough analyser, the adsorbent is packed into a column, through which gas and vapour mixtures – either pure species in a carrier gas or a multicomponent mixture – can be passed. A method for detecting the change in gas composition at the outlet of the column is also required. The choice of detector is dependent upon the species but quadrupole mass spectrometry is one of the more versatile options because it allows continuous sampling and is sensitive to a wide range of monatomic and light gases, as well as hydrocarbons and different isotopes. This is in contrast to most other methods, which are normally either non-selective or restricted to specific species (McNair and Miller, 2009), or require a sample to be extracted for analysis and are thus non-continuous. Dead space minimisation is also important in order to maximise response times.

A measurement is performed by first preparing the adsorbent bed via heating and degassing, or by inert gas purging. Carrier gas is then flowed through the bed and a step change in the inlet composition introduced. The composition at the outlet is monitored until breakthrough occurs. The breakthrough curve is then a plot of the composition at the outlet against time, relative to the initial inlet composition. Depending on the adsorption behaviour of the bed, an increase in the concentration will be seen at a given time, tb, known as the breakthrough time. This will depend primarily on the adsorption capacity of the column, but the shape of the curve will be determined by various other factors, including interparticle diffusion and intraparticle sorption kinetics, axial flow dispersion, and heat transfer effects.

What can they Tell Us?

For mixtures, differences in tb for each component provide a clear indication of the capability of the adsorbent to separate the components under the tested conditions of temperature, pressure, flow rate and inlet gas composition. The measurement of breakthrough curves can thus be used as a rapid method to compare the potential performance of new materials for separation applications.

Although breakthrough first occurs at tb, another parameter is the stoichiometric breakthrough time, ts, which is defined as the time taken for the outlet composition to reach 50 per cent of that of the inlet (Broom and Thomas, 2013). For a given column size, these parameters can be directly compared between materials but data can also be modelled to provide a more detailed analysis.

Why is Adsorption of Interest?

Adsorption has long been established as an effective and energy efficient alternative to other separation and purification processes - including distillation, chemical absorption and cryogenic methods. However, the choice depends on a number of factors, including the scale of the process and the availability of adsorbents with the right combination of properties, such as a high working capacity, sufficient selectivity, and good thermal, hydrothermal and mechanical stability.

Another important consideration is the required purity of the product. In some cases, adsorption has significant advantages in this respect although membrane separation

Figure 1: An automated breakthrough analyser

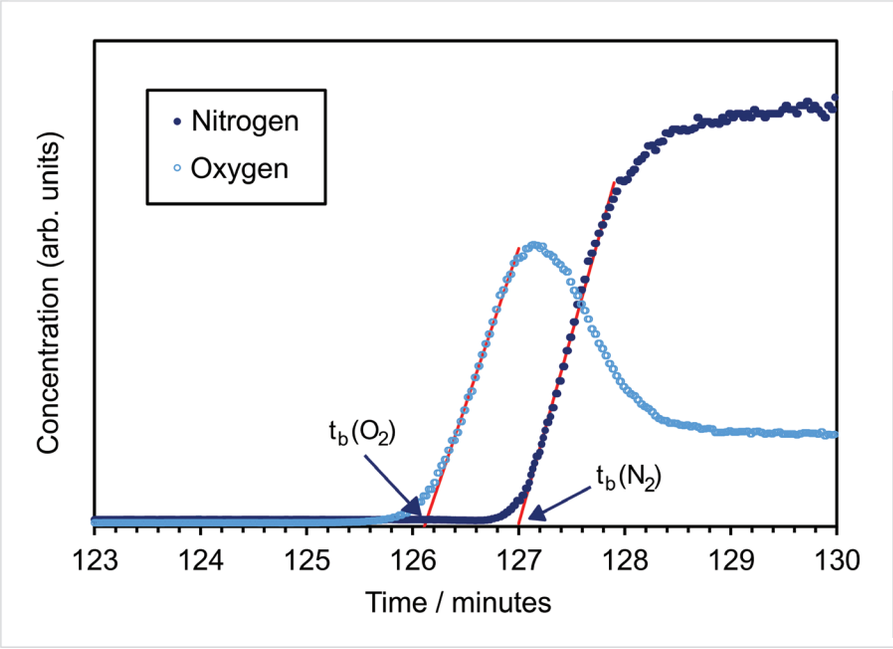

Figure 2: Breakthrough curves determined for an 80%/20% N_2/O_2 mixture at 10 bar and 25°C for 13X zeolite. The concentration is the mass spectrometer signal, in arbitrary units, for the peaks in the mass spectra at m/e = 28 (N_2) and 32 (O_2), as determined from the peak heights.

can also offer a competitive alternative (Baker, 2012). Different processes are available, including temperature swing adsorption (TSA) and pressure swing adsorption (PSA). These differ in the method used to regenerate the adsorbent (Yang, 1997). TSA involves heating, whereas PSA involves reducing either the total pressure or the partial pressure of the adsorbed component. In each case, the adsorption properties of the materials must be understood.

Which Separations Use Adsorption?

Examples of separations that already use PSA commercially include H_2 separation from syngas, N_2 and O_2 production from air, and He purification following raw or crude helium production from natural gas (Häring, 2008). In each case, the process exploits either the different equilibrium or kinetic behaviour of the gases adsorbed in microporous adsorbents such as zeolites and carbon molecular sieves.

For hydrogen production, H_2 interacts weakly with materials, whereas other typical components of syngas, which include CO, N_2, CO_2 and hydrocarbons, show a stronger interaction, and thus tend to adsorb more strongly. PSA is the main technology used for this application with over 85 per cent of the global hydrogen production units using this method for purification purposes (Sircar and Golden, 2010). Activated carbons, zeolites and silica gels are all used but new adsorbents are also under investigation. Breakthrough curves determined with H_2/CO, H_2/N_2 and H_2/CO_2 and multicomponent mixtures of these will clearly provide an indication of the ability of a new adsorbent to retain the more strongly adsorbing species.

Air separation, meanwhile, relies on different adsorption mechanisms depending on the required product. N_2 production, for example, typically uses carbon molecular sieves in which the diffusion rates of N_2 and O_2 through the pores differ considerably. On the other hand, O_2 production uses zeolites that show significantly different equilibrium uptakes for O_2 and N_2. The choice of material for this application, of course, depends on its adsorption properties, with Ca-A and low silica X (LSX) zeolites both being used commercially (Kulprathipanja, 2010, Ruthven, 2011).

For either N_2 or O_2 production applications, breakthrough curve measurements provide a rapid laboratory testing method for different materials, compared to other more laborious multicomponent techniques. As an example, Figure 2 shows data measured on 13X zeolite using an 80/20 per cent mixture of N_2/O_2 at 10 bar and 25°C, with the O_2 clearly breaking through the bed before N_2.

As for H_2, helium production and purification using adsorption exploits the weak interaction of He with materials compared to the typical components of the feed mixture, which include CH_4 and N_2. Raw or crude helium is typically produced from natural gas, in which He is present at relatively low levels as a result of radioactive decay (Häring, 2008). This typically consists of between 50 and 90 per cent He, and is produced using other processes, but PSA with zeolites or activated carbons can be used to purify the product to levels of up to 99.9999 per cent (Häring, 2008). Breakthrough curves measured using mixtures of these species will again provide important information regarding the suitability of different adsorbents for this application. As He does not interact strongly with any solid or surface, it is the working capacity of a particular material for CH_4 and N_2, combined with its cost and other practical considerations that will ultimately determine its suitability.

An emerging application, which is currently attracting a significant amount of attention, is CO_2 capture. Many new porous materials are being investigated for this purpose, including novel porous carbons, metal-organic frameworks (MOFs) and microporous organic polymers (Lu and Dai, 2014). There are two main types. Pre-combustion capture involves the separation of CO_2 from syngas that has undergone the water-gas shift reaction (Häring, 2008, Platon and Wang, 2010). This mainly involves the separation of a H_2/CO_2 mixture at an elevated pressure of a few MPa. Post-combustion capture, meanwhile, involves the separation of CO_2 from an N_2-rich flue gas at ambient pressure. Another important consideration is that flue gas often contains contaminants. It is thus important to assess the resistance of a material to species such as H_2O and sulphur-containing compounds, such as H_2S, as well as their ability to perform separations in the presence

of these impurities. All of these aspects can be investigated using breakthrough curve measurements.

Conclusion

In this article, we have introduced breakthrough curve measurement, which provides a rapid alternative to laborious multicomponent adsorption measurements for the characterisation of adsorbents for gas separation and purification applications. We have seen that breakthrough curves can provide useful information on the mixture adsorption or separation properties of porous materials, which is important during the laboratory scale assessment of new adsorbents. A number of gas separation applications that are in practical use have been discussed, and CO_2 capture used as an example of a future application that has recently been attracting a great deal of interest. ■

References

1. Baker, R. W. (2012) Membrane technology and applications, 3rd Edition. Wiley, Chichester
2. Broom, D. P., Thomas, K. M. (2013) Gas adsorption by nanoporous materials: future applications and experimental challenges. MRS Bull. 38, 412-421
3. Häring, H.-W. (ed.) (2008) Industrial gases processing. Wiley, Weinheim
4. Kulprathipanja, S. (ed.) (2010) Zeolites in industrial separation and catalysis. Wiley, Weinheim
5. Lu, A.-H., Dai, S. (eds.) (2014) Porous materials for carbon dioxide capture. Springer, Heidelberg
6. McNair, H. M., Miller, J. M. (2009) Detectors. In: Basic gas chromatography, 2nd edition. Wiley, New Jersey, p. 104-128
7. Platon, A., Wang, Y. (2010) Water-gas shift technologies. In: Liu, K., Song, C., Subramani, V. (eds.) Hydrogen and syngas production and purification technologies. Wiley, New Jersey, p. 311-328
8. Ruthven, D. M. (2011) Molecular sieve separations. Chem. Ing. Tech. 83(1-2), 44-52
9. Sircar, S., Golden, T. C. (2010) Pressure swing adsorption technology for hydrogen production. In: Liu, K., Song, C., Subramani, V. (eds.) Hydrogen and syngas production and purification technologies. Wiley, New Jersey, p. 414-450
10. Yang, R. T. (1997) Gas separation by adsorption processes. Imperial College Press, London

Author's Details

Dr Darren Broom
Product Manager
Hiden Isochema Ltd
E: dbroom@hidenisochema.com