

The Use of Adsorbed Natural Gas Technology for Large Scale Storage.

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Abstract

Considerable understanding of ANG technology has been gained from work aimed at implementing this method of storage in natural gas vehicles (NGVs). For vehicle applications, maximum gas storage density becomes the ultimate requirement to produce vehicles with an acceptable mileage range. Bulk storage applications require a number of different issues to be addressed relative to vehicle onboard storage, particularly with regard to configuration and physical properties of the adsorbent. A complex compromise of cost versus performance is required which leads to a very different technology configuration than would be expected for vehicles.

1 Introduction

Adsorbed natural gas (ANG) provides a method of storing gas at a substantially higher concentration than can be achieved with simple compression. Although not attaining the density typically found with methods such as LNG, it is potentially much simpler, not requiring the use of refrigeration methods or significant ancillary equipment. Although adsorption on carbon materials developed to date produces its greatest *absolute* enhancement at pressures around 35 bar, higher *relative* gains are obtained in the 3-10 bar range more appropriate to local storage and distribution systems.

Considerable experience of ANG technology has been gained from work on natural gas vehicles (1). For vehicle applications, maximum gas storage density becomes the ultimate requirement, in order to produce vehicles with an acceptable mileage range. To this end, a great deal of research effort has been expended to try and produce active carbons capable of storing up to 190 volumes of gas per volume of storage space (v/v) at pressures of approximately 35 bar. This research has led to the production of some extremely highly engineered carbon materials.

Bulk storage applications require a number of significantly different issues to be addressed in comparison to onboard vehicle storage, particularly configuration, cost and nature of the adsorbent. For bulk storage applications, the viability of the method is critically dependent on the cost of the adsorbing material. Thus although considerable gains can be made in storage capacity by choosing a high performance carbon, the price tends to increase disproportionately to the advantage gained. In addition, high performance carbons tend to have high densities. High density carbons will occupy a smaller volume in the storage vessel; as carbons are priced by weight, there is a proportional rise in cost with increasing density. A compromise in cost/performance is therefore required which leads to a very different choice of carbon for large scale carbon compared to small scale vehicle applications.

This paper will give an overview of work at BG Technology which looks at the feasibility of applying ANG to large scale storage of natural gas

2 The Technical Challenges

Adsorption isotherms in physical chemistry are generally expressed as concentration of adsorbed phase per unit mass of adsorbent. For ANG applications we are concerned with the storage per unit volume. As a result, the density of the adsorbent becomes increasingly important. The storage capacity under these circumstances is usually expressed in terms of volume per volume stored (v/v). This expresses the enhancement in capacity of a particular volume of storage medium relative to an empty container at standard temperature and pressure.

2.1 Carbon development and the adsorption process

Activated carbon is made from cheap natural products such as coconut shells or peach stones. They are subjected to either chemical impregnation followed by heating, or are first pyrolysed to carbon and then subjected to steam treatment. As such they have an extremely high surface area (up to 2500m²/g) and pore sizes as low as 2 nanometres. A typical carbon will be a mixture of small micropores, larger macropores, mesopores from which the gas can escape, and void space. The distribution of these governs the storage capacity of the carbon and is dependent on the preparation

process. The carbon itself can be produced as powder, granules or formed into monoliths or briquettes. Highly activated carbons, and shaped and densified materials have the highest storage capacities, but the increased number of steps required in preparation can push costs per kg very high. Theoretical enhancements of the order of 270 v/v are possible, but practically, the best seen so far are around 150 v/v. Doubling capacity from 75 to 150 v/v at 35 bar can potentially lead to a 20 fold increase in the cost per kg of the carbon. Such monolithic carbons are ideal for vehicle applications where maximum storage capacity is critical and the cost of the carbon is a relatively small part of the overall process. However, as already stated, the excessive cost mitigates against their use for bulk storage. For large scale storage applications, the carbon used is more likely to be in the 80-100 v/v range.

2.2 Deliverability

Any discussion of adsorbed natural gas should make clear that it is not simply the storage capacity of the system which is being considered. *More important is the quantity of gas which can be delivered on desorption.* The storage capacity of an ANG system is always greater than the delivered capacity, usually by around 15%, but sometimes by as much as 30%. The nature of adsorption on microporous systems leads to a large extent of capacity being filled at atmospheric pressure. The amount of gas remaining on the carbon under atmospheric conditions is around 10 times that which would be present in an empty vessel. This gas cannot be discharged from the vessel without reduction in pressure, or displacing it with a more strongly adsorbing gas. The amount of gas which remains in the system is highly dependent on the carbon used. Highly microporous carbons have very steep initial slopes to their uptakes, and therefore retain a larger proportion of the gas on delivery. Careful choice of carbon is necessary to minimize the quantity of retained gas, particularly if use is to be made of ANG in relatively low pressure systems.

2.3 Heat management

The extent of uptake on an adsorbent reduces with increasing temperature, so warming of the system is likely to lead to reduced uptake. Adsorption is of course a process which evolves heat. Due to the highly thermal insulating nature of the carbon material, in a large storage vessel the degree of equilibration of the system with its surroundings is likely to be limited during a typical 8 hour fill. Although filling a completely gas free ANG vessel can produce enough heat to increase temperatures by up to 100°C in a perfectly insulated vessel, it should be borne in mind that in practice this is not the case. At the start of the fill cycle at 0 barg or 1 bara, there is already a layer of adsorbed gas on the carbon, as discussed in the previous section. Adsorption at these initial sites tends to produce the highest heat of adsorption. As anything up to 30% of the total capacity of the bed is present in this non-delivered gas, the total amount of heat released during a typical fill is considerably reduced.

It should also be borne in mind that the total amount of gas stored within a carbon or other adsorbent under pressure is not simply the amount adsorbed in the micropores. This ignores the contribution made by the natural gas in the voids and larger pores where it is stored at the gas phase density of the adopted storage pressure. For a promising carbon, up to 25% of the stored methane can be present as pressurised gas in the voids and therefore contributes no heat of adsorption. Temperature rises of 40-50°C are in fact more likely during a typical fill.

A similar analysis can be used to consider the cooling effect of desorption, where temperatures can drop extensively. The main problem this can cause is in the ease of delivery of the gas at the lowest temperatures, where the rate of desorption will slow.

The experimental programme currently underway indicates that the average carbon temperature is likely to oscillate between -10°C and 40°C, with wall temperatures only varying between 12-25°C. Prevailing environmental conditions during fill and discharge phases are likely to benefit temperature effects during the diurnal phases, as the external temperature is likely to be warmest during delivery of gas when heat is required, and coolest during the fill, when heat is evolved.

2.4 Gas composition

The composition of natural gas varies widely and it always contains gases other than fuel gases, for example, odorant, higher hydrocarbons, CO₂ and N₂. Whereas the adsorption capacity for methane in ANG systems remains constant throughout many adsorption and desorption cycles, such cyclic operation using real natural gas would result in a gradual deterioration of capacity (2,3). This

problems caused by heat transfer during diurnal cycles, and also to issues relating to use of natural gas rather than pure methane. The experimental programme should also allow the tailoring of carbon properties to the requirements of diurnal storage applications, and also allow determination of the ideal internal configuration of the vessel. This latter issue relates particularly to extra methods which may have to be used to cope with problems of heat management.

A development programme was implemented which included parallel experimental work and development of a numerical model.

3.2 The experimental rig

The experimental facility (fig 2) is based around a 500dm³ carbon steel pressure vessel, which has been equipped with 24 positioned thermocouples, internal and external, and 2 internal pressure transducers. The vessel has full bore flanged covers top and bottom and has been designed to allow it to be rotated through 90° to allow measurements to be taken in both upright and horizontal configurations. It is rated up to 40 bar and over a 180°C to -30°C pressure range. Flow into and out of the vessel is controlled using 200dm³/min flow controllers. Temperature, flow and pressure data are continuously logged during experimental runs using a National Instruments 'Labview' based system.

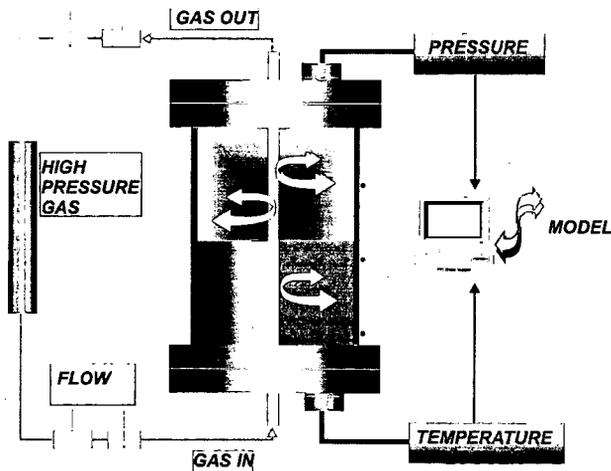


Fig 2. Schematic of experimental rig for cyclic diurnal simulation

3.3 The numerical model

The cylindrical rig has been modelled in its axial and radial dimensions form using a finite difference (explicit scheme) program written in Fortran 90. The model comprises a steel outer shell and a steel inner tube, together with the carbon bed. A single element is assumed to be at equilibrium at a single temperature and the carbon bed pressure is therefore uniform. Conduction is modelled in two dimensions but mass flow (and consequently its associated convective heat transfer) is only allowed in the radial direction. Loading of methane onto the carbon bed, desorption from the bed and the static situation (with no net gain or loss of gas) can be simulated, together with combinations of these phases as is the case in practice. The fit of a simulated run to an experiment involving loading and desorption with a static period in-between is shown in Figure 3.

3.4 Illustrative results

Fig 3 show a subset of data from a simulated diurnal cycle in the 500dm³ vessel, using a commercial carbon material. Only temperature and pressure data are shown here for simplicity. The thermocouples from which these data were obtained were situated in the bulk of the carbon. Close agreement is obtained between experimental and simulated data. Other sets of thermocouples,

deterioration is the result of accumulation of the impurity gases on the adsorbent used because of the preferential adsorption of the heavier hydrocarbon gases.

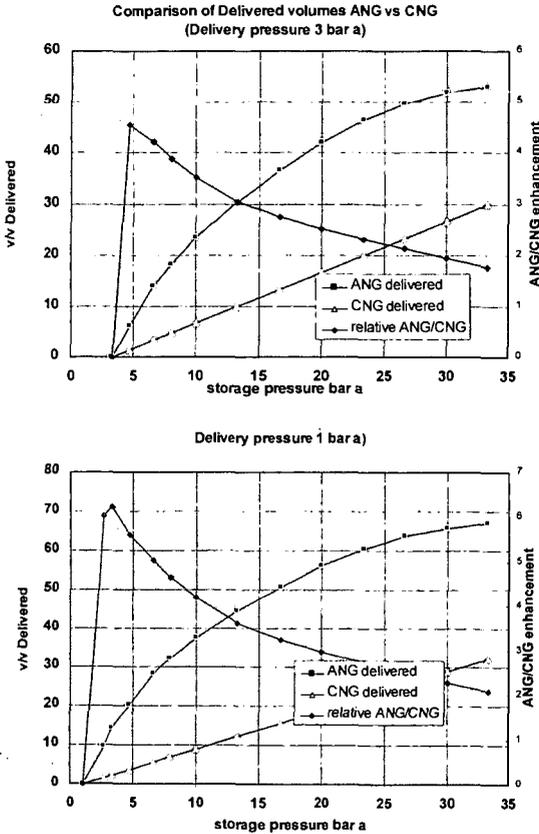


Fig 1. Delivered gas curves for a commercial carbon for different base pressures.

This problem has been addressed in NGV work by the use of some form of preadsorption system to remove the heavier hydrocarbon gases prior to adsorption in the main storage tank. All hydrocarbons adsorb more strongly on carbon than methane, as do the odorants added to natural gas (4,5). One component of natural gas which may require special treatment is water, which although only present at ppm levels in distributed natural gas, tends to adsorb strongly. Experimental work currently under way aims to determine the necessary physical and operating characteristics of a preadsorbing system to protect the main carbon bed.

3 Work in the BG Technology Programme

3.1 Philosophy of work programme

Work is currently underway to estimate the merits of ANG technology for large scale and diurnal storage applications. Techno-economic analyses appeared to indicate that there was a good probability that cost targets for technology use could be met. An experimental programme was initiated to provide predictive data for scale up. These data relate particularly to the extent of any

placed at the vessel core, vessel inner and outer walls and vessel inlet and outlet show corresponding agreement with modelled data. Uptakes of gas were also measured and modelled as a function of time, again with close agreement, but are not illustrated here. The major outcome of this work is the illustration that a real diurnal storage case can be effectively modelled, and current work is extrapolating these data to large scale cases for a variety of practical scenarios.

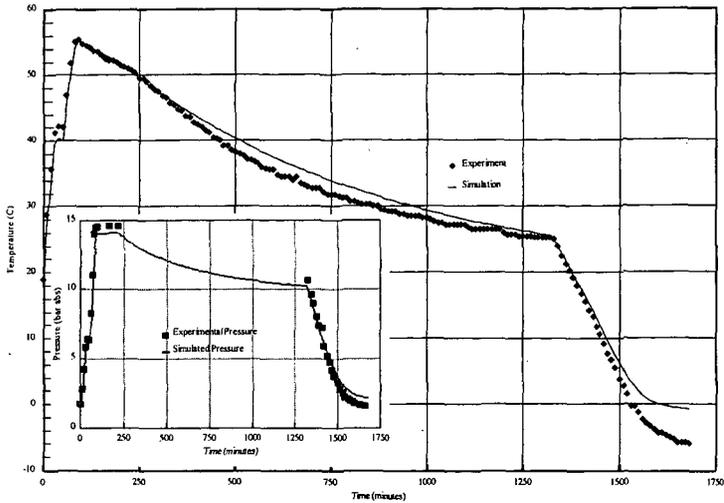


Fig 3. Illustrative data from experimental run and model.

4 Conclusions

The ANG storage method can provide enhancements over pressurisation of the order of 2-10 times depending on storage pressure. Relative gains over pressurisation are greatest at lower pressures, although the absolute amount of gas stored increases with pressure. Delivered rather than stored gas needs to be optimised in order to gain maximum benefit from the technique. The economics of the process depend critically on the choice of carbon adsorbent. Lower density carbons with low cost and high performance are preferred. A compromise between these factors will be required to obtain the most favourable implementation. Adsorbent lifetimes should not be a problem, as long as care is taken to prevent adsorption on the main bed of components which could irreversibly adsorb and degrade performance.

5 References

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