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Automatic Filtering and Reodorization of Adsorbed Natural Gas Storage Systems

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Abstract. The presence of high molecular weight hydrocarbons and sulphur-based odorants in natural gas has a negative impact on the storage of this fuel using adsorption technology. The reason for this is the deterioration of the adsorbent capacity on extended cyclic operation. Although a good adsorbent is key to the success of ANG, its potential will be limited if it is not integrated into a well-designed system which compensates for the weakness inherent in the adsorption process, deleterious poisoning and heat effects. Although there appears to be a consensus on the use of a especially tailored carbon-based filter or guard-bed to prevent the contamination of the storage tank, this system has not yet been studied or evaluated in real depth. In this work, it is demonstrated for the fist time that it is indeed possible to filter and reodorize the delivered natural gas using a properly operated carbon-based filter.

Keywords: natural gas, adsorption storage, activated carbon, guard bed

1. Introduction

The decrease in storage capacity of the adsorbent with the number of cycles is undoubtedly one of the most important problems in vehicular and large-scale applications of adsorbed natural gas (ANG) storage. If the impurities are not prevented from entering the storage tank during filling, they tend to accumulate from cycle to cycle until adsorption/desorption equilibrium is reached (Mota, 1999). This can lead to a significant decrease in adsorbent storage capacity. Furthermore, in the case of large-scale stationary storage safety standards require that the gas be properly odorized when delivered to the consumer.

The use of a well-designed guard bed, which itself is an adsorbent system, with a carefully selected adsorbent for rapid preferential adsorption of the higher molecular weight components, is effective at maintaining the storage capacity of an ANG storage system. Detailed information, which relates directly to the design, effectiveness and operation of carbon guard beds in ANG, is somewhat scarce (Cook et al., 1999). The desirable characteristics of active carbons for guard-bed applications, the design of the guard bed itself, e.g., fixed or mobile, and its method of operation, i.e., heated or non-heated, have not yet been studied or evaluated in real depth.

The proposed filtering system was developed within an European project,[1] its method of operation is sketched in Fig. 1. The discharged stream from the main storage tank is heated dynamically before being fed to the guard bed so that the odorants are released at a prescribed concentration. The control scheme applies a pre-computed optimum temperature ramping to the heated gas, while simultaneously manipulating the bypass flow rate to achieve the best possible reodorization. This control strategy has been incorporated into the control module of the pilot-scale guard-bed system. The control module, was implemented as a dynamic linking library (DLL) and communicates with the Labview data acquisition and control software to update the values

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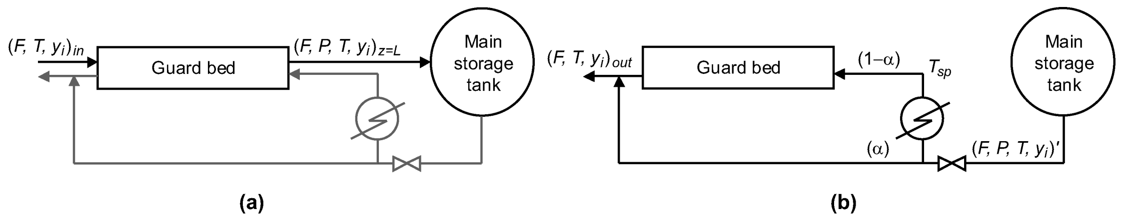

Figure 1. Schematic diagram of the two-step operation of the ANG storage system: (a) charge step, (b) discharge step. α is the bypass flow fraction and T_{sp} is the temperature of the heated gas; both variables can be manipulated during discharge.

of the manipulated variables based on the measured data.

2. Adsorption of Natural Gas Components on Activated Carbon

The adsorbent employed in the guard bed is a coal based, high activity (109%CTC), extruded carbon (2 mm diameter pellets) from Sutcliffe Speakman Carbons, Ltd. (UK). The pore structure of the carbon was characterized using standard N_2 adsorption and mercury porosimetry (Table 1). The chemistry of the carbon surface was analyzed by the PZC method and Boehm titration.

The gases selected for study are the n-alkanes C_1–C_4, N_2, CO_2, and tert-butyl mercaptan (TBM) and tetrahy-drothiophene (THT), which are two of the more widely used sulphur odorants for natural gas in Europe. This set of gases is the basis for establishing a multicomponent adsorption model of a real natural gas. Their adsorption equilibria on the carbon adsorbent were measured gravimetrically using a high-pressure magnetic suspension balance from Rubotherm (Germany), driven with in-house-developed Labview software. The odorant isotherms, in the concentration range 0–750 mg/Nm^3, were measured using a continuous-flow gravimetric method. Each measurement consisted of exposing the adsorbent sample to the isothermal flow of a calibrated mixture of the odorant diluted in helium (6.74 ppmv), at a constant pressure in the range 0.1–30 bar. Tests with pure helium showed that its adsorption was negligible compared with that of the odorants, even at the low partial pressures considered in this work, and that it could be safely used as the carrier gas without the need for correction of the results.

Table 1. Characterization of carbon sample by N_2 adsorption at 77 K and mercury porosimetry.

BET surface area, m^2/g	1342	Mercury porosimetry	
Total pore volume (0–200 Å), cm^3/g	0.850	Total pore volume (20–10^5 Å), cm^3/g	0.881
Micropore volume (0–20 Å), cm^3/g	0.777	Mesopore volume (200–500 Å), cm^3/g	0.413
Narrow micropore volume (0–6 Å), cm^3/g	0.367	Macropore volume (500–10^5 Å), cm^3/g	0.468
Broad micropore volume (6–20 Å), cm^3/g	0.410		

The experimental adsorption data were successfully correlated by the Adsorption Potential theory (Agarwal and Schwarz, 1988), using affinity coefficients, β_i, as shifting factors to collapse the data of all gases into a single characteristic curve. The affinity coefficients of the supercritical gases were determined experimentally; those of the vapors were computed using the correlation proposed by Wood (1992, 2001), which employs the molecular parachor as parameter. To obtain a workable isotherm model for process simulation, the experimental characteristic curve was fitted by the Dubinin-Astakhov (D-A) equation. This isotherm model is compared directly to the experimental adsorption data in Fig. 2, which also displays the experimental characteristic curve obtained and the β_i values employed to generate it. The plots show that there is good agreement between model predictions and the experimental data for all of the adsorbates.

3. Dynamic Model of the ANG Storage System

The guard bed is adequately described by a non-isothermal and variable-velocity axially dispersed plug-flow model, with a linear driving force rate model used for particle uptake. For brevity, we do not reproduce the model equations here and, instead, concentrate on the coupling between the guard bed and the main storage tank. The momentum equation is assumed to be given by steady-state Ergun's law, which

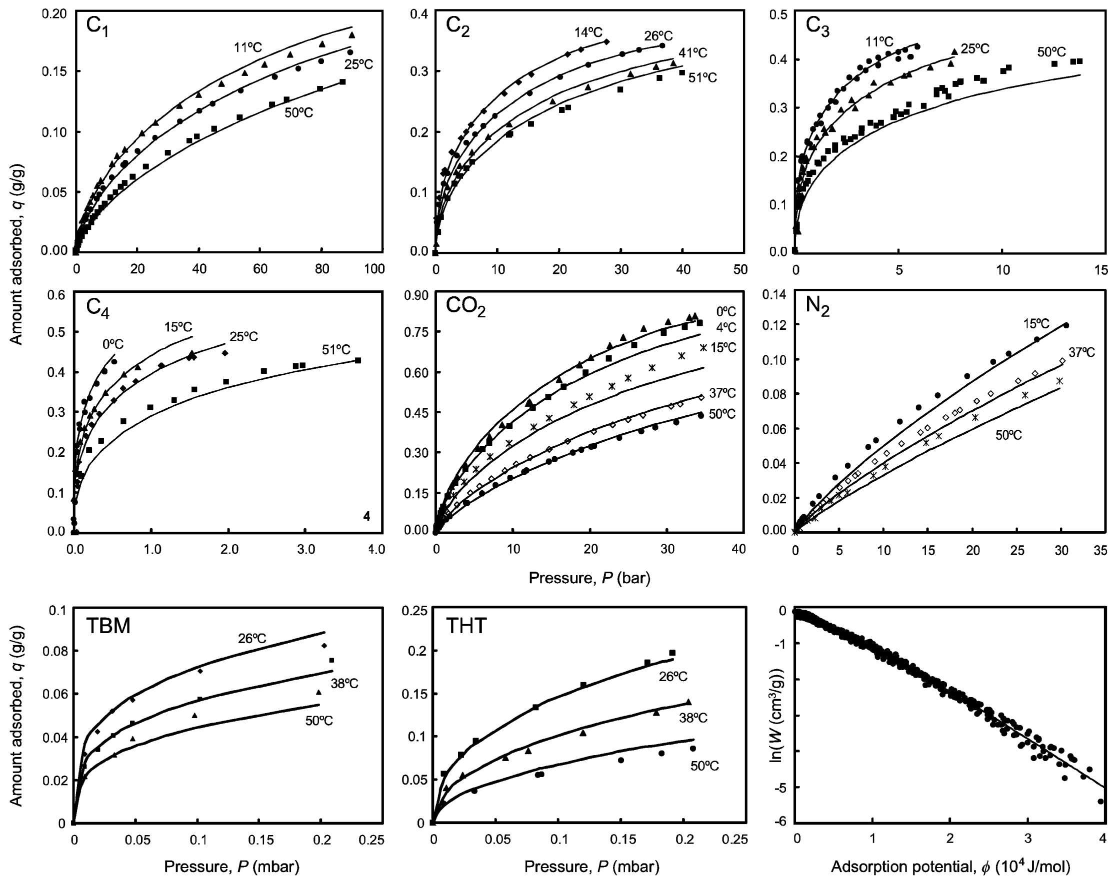

Figure 2. Experimental single-component isotherms and characteristic curve for adsorption of the *n*-alkanes C_1–C_4, CO_2, N_2, TBM and THT, on activated carbon. Symbols denote experimental data and lines represent predictions from the D-A isotherm model with affinity coefficients $\beta_{C1} = 0.47$, $\beta_{C2} = 0.63$, $\beta_{C3} = 0.78$, $\beta_{C4} = 0.86$, $\beta_{CO_2} = 0.42$, $\beta_{N2} = 0.38$, $\beta_{TBM} = 1.05$, $\beta_{THT} = 0.84$. The average error is: alkanes, 6.4% (364 data points); CO_2, 5.3% (117 points); N_2, 8.7% (66 points); TBM, 4.1% (21 points); THT, 6.8% (25 points).

upon rearrangement can be written explicitly for the fluid velocity (Mota et al., 1995). A separate spatially distributed energy balance equation for the cylinder wall is also included. The Ideal Adsorbed Solution theory (Myers, 1989) is employed as a thermodynamically consistent method of extending the D-A isotherm model to multicomponent adsorption. This can be done very efficiently, as described elsewhere (Rodrigo and Mota, 2001). There is experimental evidence that for the *n*-alkanes series this can be done using the Adsorption Potential theory, as demonstrated recently by Holland et al. (2001) on Westvaco BAX-1100 carbon, and assumed previously by us (Mota, 1999).

Although the main purpose of the model is to accurately predict the dynamics of the guard bed, it is necessary to take into account its interaction with the main storage tank (see Fig. 1). For that purpose, the main storage tank is modeled using a simple lumped-parameter approach in which the spatial variations are neglected. The main objective of this simplified model of the storage tank is to generate realistic pressure profiles over time during both charge and discharge. The governing equations are basically spatially-averaged versions of the detailed conservation equations of the guard bed.

We adopt the notation of primed symbols for the storage tank and unprimed ones for the guard bed. When the system is being charged, the boundary conditions that apply to the guard bed are

$$\begin{aligned} c_i v_z - \epsilon D_{iz} c \frac{\partial y_i}{\partial z} &= \frac{(F y_i)_{\text{in}}}{\pi R_w^2}, \\ c C_g v_z T - \lambda_z \frac{\partial T}{\partial z} &= \frac{(F C_g T)_{\text{in}}}{\pi R_w^2} \quad \text{for} \quad z = 0, \qquad (1) \end{aligned}$$

$$\frac{\partial y_i}{\partial z} = 0, \quad P = P', \quad \frac{\partial T}{\partial z} = 0$$
$$\text{for} \quad z = L, \tag{2}$$

where P' is the total pressure in the main storage tank and F_{in}, T_{in}, $(y_i)_{\text{in}}$ and $(C_g)_{\text{in}}$ are, respectively, the mass flow, temperature, mole-fraction composition and specific heat of the feed gas. During the charge step the pressure in the guard bed is equal to that in the storage tank.

The appropriate boundary conditions when the system is being discharged are

$$\frac{\partial y_i}{\partial z} = 0, \quad cv_z + \frac{\alpha}{1-\alpha}(cv_z)_{z=L} = \frac{F_{\text{out}}}{\pi R_w^2},$$
$$\frac{\partial T}{\partial z} = 0 \quad \text{for} \quad z = 0, \tag{3}$$
$$y_i = y_i', \quad P = P' \quad \text{or} \quad \frac{dP}{dt} = k_v(P_{\text{low}} - P),$$
$$T = T_{\text{sp}} \quad \text{for} \quad z = L, \tag{4}$$

where F_{out} is the discharge flow rate and T_{sp} is the temperature of the heated gas. If desired, during this step the pressure in the guard bed can be quickly depressurized down to the lowest operating pressure P_{low}. This operation is simulated by inserting a control valve with discharge coefficient k_v that imposes a first-order dynamics on the depressurization.

Due to the bypass, the composition of the reodorized gas is different from that of the gas leaving the guard bed at $z = 0$; its mole-fraction composition $(y_i)_{\text{out}}$, and the average deviation of its total odorant concentration from the target value, can be computed as follows:

$$(y_i)_{\text{out}} = \frac{(y_i F)_{z=0} + y_i'\alpha(1-\alpha)^{-1}(F)_{z=L}}{F_{\text{out}}},$$
$$e_{\text{od}} = \frac{1}{t_d}\int_{\text{discharge}} \frac{|(y_{\text{od}})_{\text{in}} - (y_{\text{od}})_{\text{out}}|}{(y_{\text{od}})_{\text{in}}} dt, \tag{5}$$

where $(y_{\text{od}})_{\text{in}}$ is the required odorization concentration (Fig. 1) and t_d is the discharge duration.

Due to limitations of the experimental rig at Advantica Ltd., the bypass can only be operated at pressures above $P' > 2.5$ bar. Furthermore, it is also not advisable to employ bypass flow fractions greater than about 0.9. These operational constraints are taken into account in the simulation model.

4. Control Algorithm

The temperature ramping is pre-computed off-line using the dynamic simulation model of the process coupled to a nonlinear constrained optimization package. Discrepancies between model predictions and the real process dynamics are compensated by changes to the bypass flow rate since this variable is continuously updated in feedback mode.

The hydrocarbon (HC) concentrations in the reodorized gas are monitored using a mass spectrometer at a sampling rate that is much faster than the dynamics of the guard bed. The other state variables (pressures, temperatures, mass flows, valve positions, etc.) are measured at the same sampling rate, except for the odorant (OD) concentrations. These are monitored using a gas chromatograph (GC) at a much slower sampling rate (6.4 min).

In order to eliminate the effect of the lag time of the GC on the response of the control system, an inference method was developed to predict the odorant concentrations between GC readings. Basically, the method consists of associating the OD readings to that of a reference HC whose temporal profile is employed to predict those of the odorants. The extrapolation function is updated whenever new OD readings are available. Tests showed that the best reference HC is either butane (C_4) or pentane (C_5).

Figure 3 compares the true odorant concentrations with the raw data obtained from the GC and the inferred data using the procedure described above. The lag time of the GC introduces a significant delay on the measured values of the odorant concentrations and in certain instances of the process one actually loses important information on the odorant concentration profiles. On the other hand, the odorant concentrations predicted by the inferential procedure are in very good agreement with the true values. This procedure has been implemented both in the simulation model of the storage system and in the real control module of the process.

To determine the optimum temperature profile T_{sp} of the heated gas for given operating conditions, the simulation model is coupled to a nonlinear constrained optimization package. T_{sp} is assumed to be a piecewise linear continuous function of the pressure in the storage tank. The minimization function is the average deviation of the total odorant concentration in the delivered

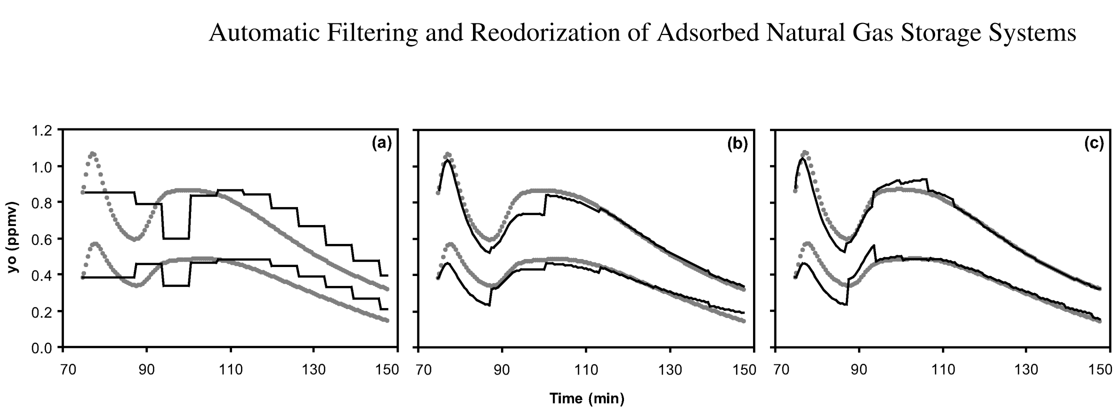

Figure 3. Comparison of true and inferred odorant readings for a simulated discharge. The gray circles denote true OD concentrations, $(y_{od})_{in}$, whereas the lines represent the corresponding sampled variables: (a) raw data sent by the chromato-graph, (b) zeroth-order extrapolation procedure, (c) first-order extrapolation procedure. The main simulation parameters are: $(y_{dms}, y_{tbm})_{in} = (0.4, 0.9)$ ppmv; $F_{in/out} = 100$ L/min; $(P_{low}, P_{high}) = (0.17, 7.0)$ barg; $\alpha = 0$; $(T)_{z=L} = 20°C$.

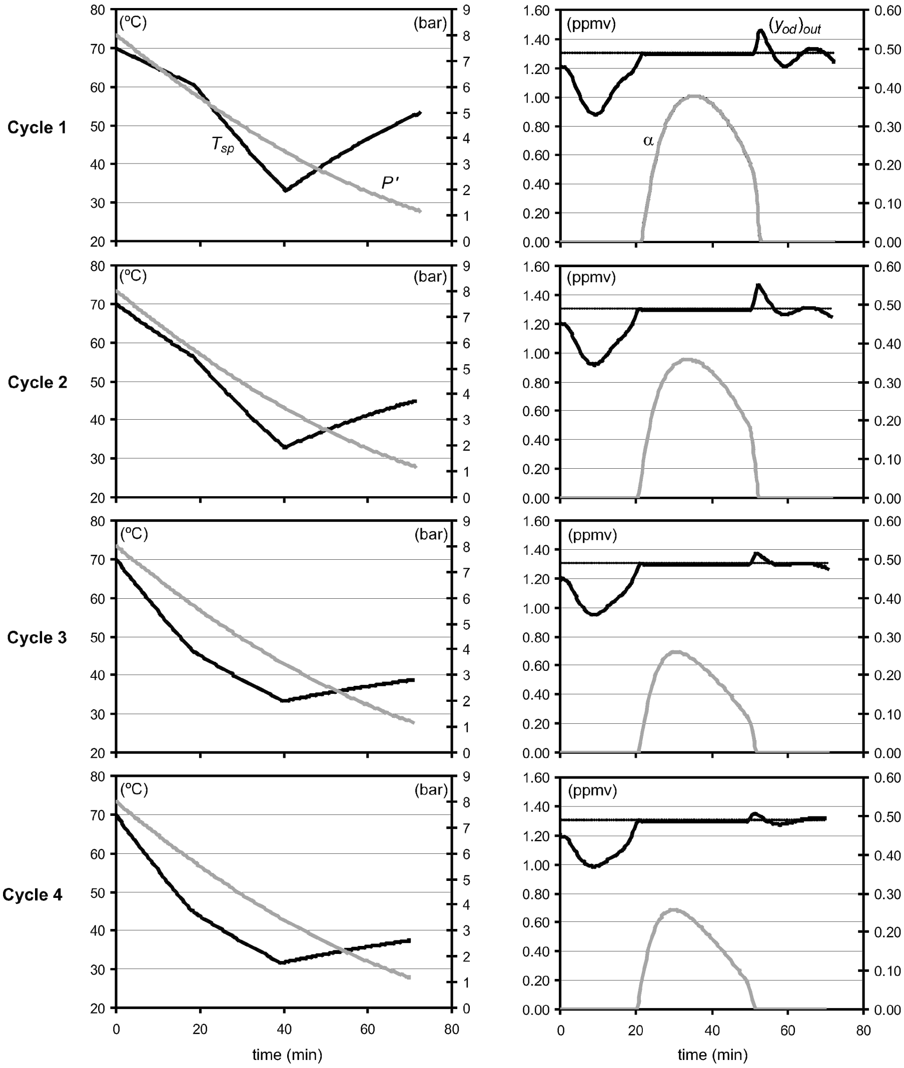

Figure 4. Computed optimum temperature and bypass profiles of heated gas for cyclic operation of the ANG storage system. The main simulation parameters are: $(y_{tht}, y_{tbm})_{in} = (0.4, 0.9)$ ppmv; $F_{in/out} = 100$ L/min; $P_{low}, P_{high} = (0.17,7.0)$ barg.

gas, e_{od} as defined by Eq. (5):

$$F_{\mathrm{obj}}(T_{\mathrm{sp}}^1, T_{\mathrm{sp}}^2, T_{\mathrm{sp}}^3, T_{\mathrm{sp}}^4) = \min_{T_{\mathrm{sp}}^1,\ldots,T_{\mathrm{sp}}^4} e_{\mathrm{od}}, \qquad 30^\circ\mathrm{C} \le T_{\mathrm{sp}}^k \le 80^\circ\mathrm{C}, \tag{6}$$

where T_{sp}^k is the temperature of the heated gas when P' attains the value

$$P_{\mathrm{low}} + (P_{\mathrm{high}} - P_{\mathrm{low}})(k-1)/3, \quad k = 1, \ldots, 4. \tag{7}$$

The optimization problem is solved using the Harwell software library package VE03. The T_{sp}^k values have been computed for various charge amounts in the range 75–125% of the nominal working value. This set of data allows the software to adjust the temperature profile to experimental conditions within that range by simple interpolation.

An example of an optimized temperature profile is plotted in Fig. 4 for the operating conditions given in the caption. The actual experiments confirmed that the optimized temperature profile, coupled with on-line compensation by means of the bypass, can smoothly desorb the odorants at the required concentration, with very little undershoot and overshot, except for the very initial stage of the discharge. This problem can be avoided by slightly pre-heating the guard bed prior to discharge.

5. Conclusions

We have briefly described a workable ANG storage process, incorporating a guard-bed for reversibly filtering out trace contaminants from the natural gas feed to the process. Based on experimental and modelling data, the system employs an advanced control scheme to allow controlled and progressive desorption of the natural gas components from the guard bed in order to achieve the desired and uniform gas composition at the outlet of the storage system.

Note

1. ANGUARD (Adsorbed Natural Gas System with Associated Guard Bed) project, supported by the 5th EU Framework Program (ENK6-CT2000-0053), led by Advantica Ltd. (UK) in partnership with Sutcliffe Speakman Carbons (UK), ISQ (Portugal), FCT/UNL (Portugal) and IPG Srl (Italy).

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