Fire and Explosion Hazards Induced by Repressurization of Air Driers

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Adsorbers used to dry or purify air typically contain 4A or 13X molecular sieves which are intermittently reactivated by thermal regeneration. This article shows that nitrogen adsorbs preferentially relative to oxygen in freshly reactivated 4A, 5A and 13X molecular sieves during the repressurization step. This produces an oxygen-enriched, high-pressure gas within the adsorber vessel which emerges immediately after the air-drier is brought on-line. The enriched oxygen concentration widens the flammability range of hydrocarbons, markedly diminishes the minimum autoignition temperature of hydrocarbons, and produces both a higher explosion pressure and a higher rate of explosion pressure rise relative to air at standard temperature and pressure. Thus, the oxygen-enriched, high-pressure gas can lead to fires, explosions, and other deleterious effects in and downstream of thermally regenerated air driers which contain large pore molecular sieves. Substituting 3A molecular sieve provides a simple, safe and inexpensive way to prevent transient oxygen enrichment and the problems associated with it. Because activated aluminas and silica gels can also enhance fire and explosion hazards, type 3A molecular sieve becomes the adsorbent of choice for air drying applications.

Introduction

Fires, explosions, and other deleterious effects in and downstream of thermally regenerated air driers provide a strong incentive to examine the operating cycle of these systems. These adsorbers frequently contain 4A or 13X molecular sieves, sometimes in combination with other adsorbents. They are used to remove small amounts of water and sometimes carbon dioxide and hydrocarbons from air streams. These adsorbers typically operate in a cycle that consists of the following steps: adsorb, depressure, heat adsorbent, cool adsorbent, and repressure. Two adsorbers are used so that one is on stream while the other is being reactivated. It has been observed in industrial practice that fires and explosions tend to occur at the start of the adsorption step, just after an adsorber vessel is brought on-line.

A thermally regenerated air drier containing 13X molecular sieve and placed between stages of an oil-lubricated compressor provides a particularly classic example. A detonation occurred in the compressor stage immediately downstream of this air drier at the start of an adsorption step. After the compressor stage was rebuilt, another detonation occurred in the same stage.

In this article we demonstrate that transient oxygen enrichment during the repressurization step and the beginning of the adsorption step contributes to both the likelihood and the severity of these accidents. While oxygen enrichment of air using molecular sieves in pressure swing adsorption (PSA) is a commercially developed technology (Ruthven, 1984; Wankat, 1986; Yang, 1987), it has not been recognized previously that oxygen enrichment also occurs in thermally regenerated air driers, nor that this oxygen enrichment can be responsible for process accidents and other undesirable effects such as accelerated oxidation leading to rust in pipes and changes in biological specimens. Although process modifications might partially alleviate the problem, substituting 3A molecular sieve for the commonly used 4A, 5A and 13X molecular sieves provides the most effective way to prevent transient oxygen enrichment and its associated problems.

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Theory

Assumptions and mass balances

Mathematical models were employed to quantify the oxygen enrichment which occurs during the repressurization and adsorption steps of thermally regenerated air driers. The assumptions include:

- The air drier operates isothermally at approximately 298 K. Both theory and industrial experience indicate that the temperature fluctuates by less than 20 K for adiabatic air driers with inlet temperatures near 298 K. A temperature fluctuation of 20 K does not affect the present results significantly. Furthermore, reliable data for nitrogen and oxygen adsorption in 4A molecular sieve are currently available only at one temperature.
- Air is considered to be a binary mixture of 79 mol % nitrogen and 21 mol % oxygen. Other trace components are neglected.
- The gas phase behaves ideally. At the highest pressure of 10 atm and lowest temperature of 297 K considered here, the compressibility factor of air is approximately 0.994. This value was calculated using the correlation of Lee and Kesler (1975), and is very close to 1.0 which describes an ideal gas.
- The gas phase exhibits plug flow during the repressurization and adsorption steps. Axial dispersion is formally neglected in the sense that the model contains no second-order derivatives.
- The axial pressure drop is negligible. In thermally regenerated air driers, the repressurization rate is small enough that the axial pressure drop can be neglected, based on the criteria developed by Sundaram and Wankat (1988). During the adsorption step, the pressure drop is typically a few psi, which is much smaller than the total pressure of 5 to 10 atm. Hence, the pressure drop during the adsorption step can be neglected also.

The mass balance for each component may be written as:

$$\epsilon \frac{\partial c_i}{\partial t} + \frac{\partial (u_o c_i)}{\partial z} + \rho_b \frac{\partial q_i}{\partial t} = 0 \tag{1}$$

where

$$c_i = y_i P/RT \tag{2}$$

The individual component mass balances may be summed to yield the total mass balance:

$$\frac{\epsilon}{RT}\frac{\partial P}{\partial t} - \frac{\epsilon}{RT^2}\frac{\partial T}{\partial t} + \frac{P}{RT}\frac{\partial u_o}{\partial z} - \frac{u_o P}{RT^2}\frac{\partial T}{\partial z} + \sum_{j=1}^{n} \rho_b \frac{\partial q_j}{\partial t} = 0 \tag{3}$$

Two different models were used to calculate $\partial q_i/\partial t$, which was substituted into Eqs. 1 and 3.

Equilibrium model

Mass-transfer resistances are assumed to be negligible in this case. Then,

$$\frac{\partial q_i}{\partial t} = \frac{\partial q^*_i}{\partial t} \tag{4}$$

As discussed below, the equilibrium model applies to thermally regenerated air driers which contain 13X or 5A molecular sieves.

Micropore diffusion-limited model

Micropore diffusion is assumed to be the rate-limiting step in this case. The two-term Glueckauf approximation (Glueckauf, 1955),

$$\frac{\partial q_i}{\partial t} = \frac{\pi^2 D_{m,i}}{R^2}(q^*_i - q_i) + \left(1 - \frac{\pi^2}{15}\right)\frac{\partial q^*_i}{\partial t}, \tag{5}$$

where

$$\frac{\partial q^*_i}{\partial t} = \frac{\partial q^*_i}{\partial P}\frac{\partial P}{\partial t} + \frac{\partial q^*_i}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial q^*_i}{\partial y_i}\frac{\partial y_i}{\partial t} \tag{6}$$

is used because it provides much more accurate results than the celebrated linear driving force approximation. As discussed below, this model applies to thermally regenerated air driers which contain 4A molecular sieve.

Adsorption of nitrogen and oxygen in molecular sieves

Adsorption isotherms are required to apply these models. Data for nitrogen and oxygen adsorption in 4A (Na-A), 5A (Ca-A) and 13X (Na-X) molecular sieves were obtained from Shen et al. (1981), Vereist and Baron (1985), and Miller (1987), respectively. The adsorption equilibria were correlated with a multicomponent Langmuir isotherm which allows for competitive adsorption:

$$q_i = \frac{a_i y_i P}{1 + \sum_{j=1}^{n} b_j y_j P} \tag{7}$$

The multicomponent (competitive) Langmuir isotherm accurately reproduces the data for air adsorption in 5A and 13X molecular sieves (Vereist and Baron, 1985; Miller, 1987), and we assume that with the appropriate parameters it provides an accurate description of air adsorption in 4A molecular sieve also. Values of the Langmuir isotherm parameters for nitrogen and oxygen adsorption in 4A, 5A and 13X molecular sieves are listed in Table 1. The nitrogen and oxygen adsorption equilibria in these large pore molecular sieves at 298 K are remarkably similar. Physical properties of these molecular sieves were obtained from data sheets furnished by the Davison Chemical Division of W.R. Grace & Co. (1986), and are also listed in Table 1.

In a series of careful experiments, Peterson (1980) showed that 1 to 5 wt. % of presorbed water greatly reduces the extent of nitrogen adsorption in 4A, 5A and 13X molecular sieves. This is a small amount of adsorbed water; these molecular sieves contain roughly 25 wt. % adsorbed water at saturation. Apparently, water adsorbs preferentially on sites near the entrances to the molecular sieve cavities, which hinders or prevents access of nitrogen molecules to adsorption sites within the molecular sieve cavities. The data and corresponding Langmuir isotherms for nitrogen adsorption in 4A (Shen et al., 1981), 5A (Vereist and Baron, 1985), and 13X (Miller, 1987)

Table 1. Parameters for Nitrogen and Oxygen Adsorption in and Physical Properties of 4A, 5A and 13X Molecular Sieves*

	4A Molecular Sieve	5A Molecular Sieve	13X Molecular Sieve
Temperature, K	297	298.55	298.15
Nitrogen:			
a_i, mol/kg/(N/m^2)	3.3750×10^{-6}	3.7550×10^{-6}	3.5180×10^{-6}
b_i, m^2/N	8.6068×10^{-7}	1.7730×10^{-6}	1.2384×10^{-6}
Micropore Diffusivity at 297 K, m^2/s	1.82×10^{-14}	**	**
Oxygen:			
a_i, mol/kg/(N/m^2)	1.0212×10^{-6}	1.1960×10^{-6}	1.0507×10^{-6}
b_i, m^2/N	0.0	4.3000×10^{-7}	1.5940×10^{-7}
Micropore Diffusivity at 297 K, m^2/s	8.25×10^{-14}	--	--
Bulk Density, kg/m^3	721	705	689
Interparticle Void Fraction	0.37	0.37	0.37

*Nitrogen and oxygen do not adsorb in 3A molecular sieve because the micropores are too small.

**Micropore diffusivities at 298 K of nitrogen and oxygen in fresh 5A and 13X molecular sieves with no presorbed water are too rapid to be measured readily.

molecular sieves were compared with the data of Peterson (1980) in the overlapping pressure range of 0 to 1 atm to check if the data were affected by presorbed water. This comparison verified that the data for nitrogen adsorption (and by inference, the data for oxygen adsorption) acquired by Shen et al. (1981), Vereist and Baron (1985), and Miller (1987) were obtained in fresh molecular sieves with no presorbed water.

Mass-transfer resistances

There are three kinds of mass-transfer resistances in thermally regenerated air driers which contain molecular sieve: micropore diffusion, macropore diffusion, and an external film resistance surrounding the molecular sieve pellets. The external film and the macropore diffusion resistances are identical for equal-size pellets of 4A, 5A and 13X molecular sieves; only the micropore diffusivities vary.

For 4A molecular sieve, we used the micropore diffusivities of nitrogen and oxygen measured by Haq and Ruthven (1986a), as shown in Table 1. With an average zeolite crystal radius of 1.3×10^{-6} m, the time scale for micropore diffusion (Glueckauf, 1955),

$$\tau_{m,\,i}=\frac{r_z^2}{\pi^2 D_{m,\,i}}, \tag{8}$$

of nitrogen and oxygen in 4A molecular sieve equals 9.4 and 2.1 seconds, respectively. These time scales are comparable to or greater than other relevant time scales in the process, and hence micropore diffusion should be included in the analysis of air driers which contain 4A molecular sieve. We note that Haq and Ruthven (1986a) measured the nitrogen and oxygen diffusivities in fresh 4A molecular sieve with no presorbed water. Like the nitrogen and oxygen adsorption equilibria, small amounts of presorbed water severely restrict both nitrogen and oxygen diffusion in 4A molecular sieve (Haq and Ruthven, 1986a; Barrer, 1978). Presorbed water probably accounts for much of the variation in the reported micropore diffusivities on nitrogen and oxygen in 4A molecular sieve.

For fresh 5A molecular sieve with no presorbed water, micropore diffusivities of nitrogen and oxygen were too rapid to measure chromatographically (Haq and Ruthven, 1986b). Laboratory experiments of pressure swing adsorption processes demonstrate that mass-transfer limitations play an insignificant role in the separation of oxygen and nitrogen over 5A molecular sieve (Fernandez and Kenney, 1983; Kayser and Knaebel, 1986; Matz and Knaebel, 1987). In all of these studies, the investigators quantitatively explained the behavior of pressure swing adsorption processes with isothermal, equilibrium models. It is important to recognize that pressure swing adsorption processes have very short cycle times (typically a few minutes) compared with the cycle times of thermally regenerated adsorption processes (typically several hours). Hence, micropore diffusion limitations of nitrogen and oxygen in 5A molecular sieve should be even less significant in the thermally regenerated air driers considered herein.

The micropores in 13X molecular sieve are approximately twice as large as those in 5A molecular sieve. The diffusivities of nitrogen and oxygen in the micropores of 13X molecular sieve should exceed those in 5A molecular sieve; indeed, they are too rapid to measure with current techniques (Ruthven, 1984). Thus, limitations resulting from nitrogen and oxygen diffusion in the micropores of 13X molecular sieve will play an insignificant role in thermally regenerated air driers.

The time scale for macropore diffusion is defined by (Glueckauf, 1955):

$$\tau_{M,\,i}=\frac{r^2}{\pi^2 D_{M,\,i}} \tag{9}$$

The effective macropore diffusivities of nitrogen and oxygen were calculated using established guidelines (Ruthven, 1984; Yang, 1987). Specifically, the effective macropore diffusivity of each species was set equal to one-tenth of the standard macropore diffusivity to account for the internal porosity of the pellets and the tortuosity of the macropores. The standard macropore diffusivity was estimated by assuming that molecular and Knudsen diffusion occur in parallel. The molecular diffusivity of N_2-O_2 was obtained from the data presented by Weissman and Mason (1962). An average macropore radius of 2×10^{-7} m (Ruthven, 1984) was used to estimate the Knudsen diffusivity. For 1/16-in.-dia. (1.6-mm-dia.) pellets, the time scale for macropore diffusion of nitrogen and oxygen in 4A, 5A and 13X molecular sieves increases to approximately 0.33 s as the total pressure increases to 10 atm. This time scale for macropore diffusion is typically much less than the repressurization time and the space time (L/u_o) for thermally regen-

Table 2. Boundary and Initial Conditions*

Process Variable	Boundary Condition for Repressurization Step	Boundary Condition for Adsorption Step
$\frac{u_o(t, z=L)}{L}$	$= 0.0\ s^{-1}$	$0.05\ s^{-1}$
$y_{N_2}(t=0, z)$	$= 0.79$	Composition at end of repressurization step
$y_{N_2}(t, z=0)$	$= 0.79$	0.79
$P(t, z)$	$= P(t)$ given by the repressurization rate of 0.01 atm/s and initial pressure of 1.0 atm	Pressure at end of repressurization step

*The bed and feed temperatures were set equal to 297 K, 298.55 K, and 298.15 K for adsorbers containing 4A, 5A and 13X molecular sieve, respectively.

erated air driers, and hence macropore diffusion in 4A, 5A and 13X molecular sieves can be neglected (Doong and Yang, 1986; Cen and Yang, 1986).

The Biot number for mass transfer expresses the ratio of internal to external mass-transfer resistances for an adsorbent pellet (Ruthven, 1984; Yang, 1987). The Biot number for mass transfer is typically over 100 for thermally regenerated air driers containing 4A, 5A or 13X molecular sieves. Thus, the external mass-transfer resistance is negligible.

To summarize, the equilibrium model applies to thermally regenerated air driers which contain 13X or 5A molecular sieve. Mass-transfer resistances to nitrogen and oxygen adsorption can be neglected. For thermally regenerated air driers which contain 4A molecular sieve, micropore diffusivity limits the adsorption rate of nitrogen and oxygen. The two-term Glueckauf approximation can be used to analyze thermally regenerated air driers which contain 4A molecular sieve.

Algorithm

The appropriate model equations were integrated numerically using backward finite differences in space and a fourth-order Runge-Kutta algorithm over time (Carnahan et al., 1969). The two-term Glueckauf approximation required only a few additional lines of FORTRAN code relative to the equilibrium model, so it is probably worth going to the complexity of this mass-transfer-limited model in the case of 4A molecular sieve. Table 2 lists the boundary and initial conditions for the repressurization and adsorption steps. The numerical solutions obtained with 50 equilibrium stages are mathematically similar to incorporating typical external mass-transfer resistances and axial dispersion into the model (Wen and Fan, 1975; Ruthven, 1984).

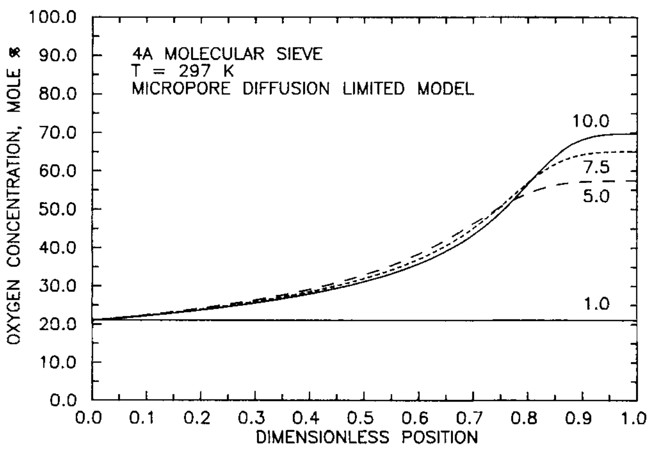

Figure 1. Predicted axial composition profiles after isothermal repressurization of a thermally regenerated air drier containing 4A molecular sieve.

The adsorber was assumed to contain freshly reactivated 4A molecular sieve and air at the start of the isothermal repressurization step. Air at 297 K entered the adsorber during the isothermal repressurization step and the simulation was continued until the total pressure in the adsorber reached 5.0, 7.5 or 10.0 atm.

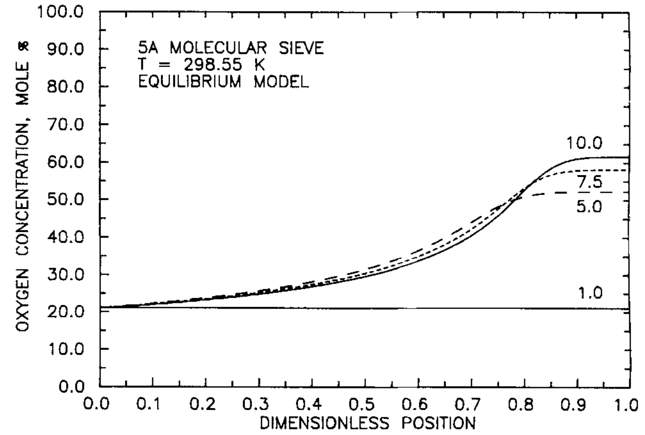

Figure 2. Predicted axial composition profiles after isothermal repressurization of a thermally regenerated air drier containing 5A molecular sieve.

The adsorber was assumed to contain freshly reactivated 5A molecular sieve and air at the start of the isothermal repressurization step. Air at 298.55 K entered the adsorber during the isothermal repressurization step and the simulation was continued until the total pressure in the adsorber reached 5.0, 7.5 or 10.0 atm.

Results

Thermally regenerated air driers which contain 4A, 5A or 13X molecular sieve

Figures 1 through 3 show the predicted axial composition profiles at the end of the isothermal repressurization step for thermally regenerated air driers containing 4A, 5A and 13X molecular sieve, respectively. In all cases, the adsorbers were assumed to contain freshly reactivated molecular sieve and air at 1 atm at the start of the repressurization step. Air entered the adsorber during the isothermal repressurization step and the simulation was continued until the total pressure reached 5.0, 7.5 or 10.0 atm. Figures 1 through 3 look very similar; they all exhibit an oxygen mole fraction of roughly 60% at the closed (effluent) end of the adsorber.

Figures 4 through 6 show the breakthrough curves that emerge from the thermally regenerated air driers during the subsequent isothermal adsorption step. The dimensionless time on the horizontal axis equals the number of bed volumes of gas that have passed through the adsorber, based on an empty vessel. Figures 4 through 6 resemble one another closely. When a thermally regenerated air drier which contains 4A, 5A or 13X molecular sieve is repressured, oxygen-enriched effluent

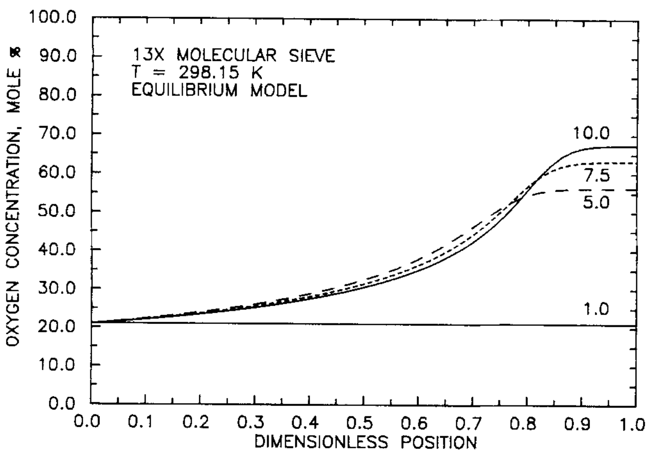

Figure 3. Predicted axial composition profiles after isothermal repressurization of a thermally regenerated air drier containing 13X molecular sieve.

The adsorber was assumed to contain freshly reactivated 13X molecular sieve and air at the start of the isothermal repressurization step. Air at 298.15 K entered the adsorber during the isothermal repressurization step and the simulation was continued until the total pressure in the adsorber reached 5.0, 7.5 or 10.0 atm.

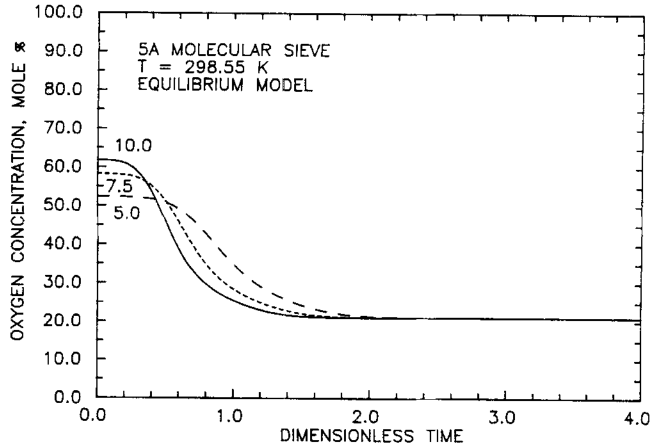

Figure 5. Predicted composition breakthrough curves for the isothermal adsorption step of a thermally regenerated air drier containing 5A molecular sieve.

Air at 298.55 K enters the adsorber during the isothermal adsorption step which immediately follows the corresponding isothermal repressurization step shown in Figure 2. The dimensionless time equals the number of bed volumes of gas which have passed through the adsorber, based on an empty vessel.

gas emerges from the adsorber during the beginning of the adsorption step. In all cases, the effluent composition returns to that of the air feed after approximately two bed volumes of air have passed through the adsorber. The nitrogen/oxygen front traverses the length of the adsorber in an amount of time approaching the space time (L/u_0) because nitrogen and oxygen are present in high gas-phase concentrations relative to the equilibrium adsorbed phase concentrations in the molecular sieves.

These results are nearly identical for 4A, 5A and 13X molecular sieves. Micropore diffusion limitations in 4A molecular sieve attenuates the oxygen enrichment and broadens the mass-transfer zone only slightly at the process conditions studied. The oxygen enrichment for 4A molecular sieve is actually greater than that indicated by Figures 1 and 4 because the two-term Glueckauf approximation underestimates the uptake of nitrogen by the adsorbent at very short times (Glueckauf, 1955). Micropore diffusion in 4A molecular sieves becomes more important, and oxygen enrichment tends to diminish with increasing repressurization rates, flow rates, and amounts of presorbed water, however.

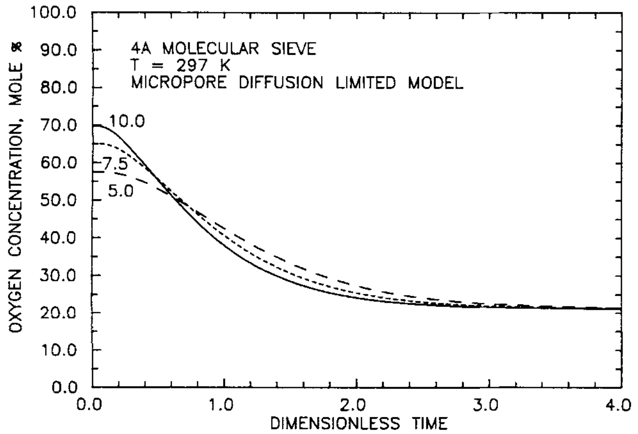

Figure 4. Predicted composition breakthrough curves for the isothermal adsorption step of a thermally regenerated air drier containing 4A molecular sieve.

Air at 297 K enters the adsorber during the isothermal adsorption step which immediately follows the corresponding isothermal repressurization step shown in Figure 1. The dimensionless time equals the number of bed volumes of gas which have passed through the adsorber, based on an empty vessel.

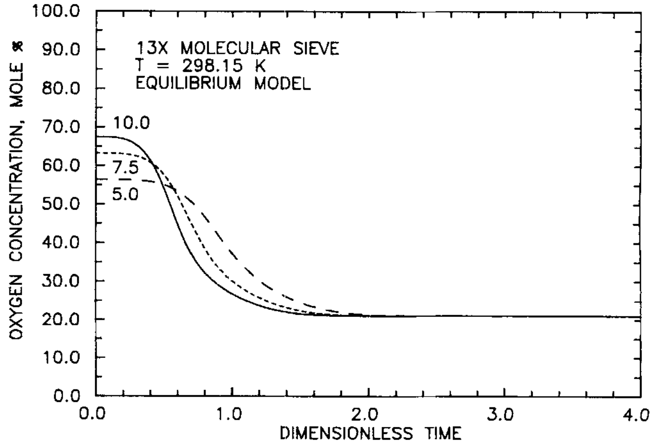

Figure 6. Predicted composition breakthrough curves for the isothermal adsorption step of a thermally regenerated air drier containing 13X molecular sieve.

Air at 298.15 K enters the adsorber during the isothermal adsorption step which immediately follows the corresponding isothermal repressurization step shown in Figure 3. The dimensionless time equals the number of bed volumes of gas which have passed through the adsorber, based on an empty vessel.

Thermally regenerated air driers which contain 3A molecular sieve

In contrast to 4A, 5A and 13X molecular sieves, neither oxygen nor nitrogen adsorbs in 3A (K-A) molecular sieve (Springer, 1964; Peterson, 1980) because the micropores are too small (Breck, 1974). Hence, oxygen enrichment and the deleterious effects it can cause will not occur in and downstream of adsorbers which contain 3A molecular sieve.

Discussion

Transient oxygen enrichment can cause problems in many applications which require dry air. Promoting combustion is a particularly dramatic example. In this section, we first discuss how oxygen enrichment exacerbates fire and explosion hazards. Then we describe how hydrocarbons, a common fuel in chemical processing equipment, may ignite in and downstream of thermally regenerated air driers. Lastly, we suggest ways to minimize transient oxygen enrichment and the problems it can cause.

Fire and explosion hazards caused by oxygen enrichment

A combination of fuel, oxidizer and a source of ignition must be present to support combustion. The presence of a high gaseous oxygen concentration widens the flammability range of hydrocarbons, markedly lowers the minimum autoignition temperature of hydrocarbons, and produces a much higher explosion pressure and rate of explosion pressure rise compared with air at standard temperature and pressure (STP). In a gaseous mixture at a given temperature, the partial pressure of oxygen rises with either an increase in the oxygen mole fraction or an increase in the total pressure. Both of these mechanisms operate during the repressurization of air driers which contain 4A, 5A or 13X molecular sieve.

Increasing the oxygen mole fraction above the 0.21 level found in air greatly expands the flammability range (Bodurtha, 1980), which is the range of hydrocarbon concentrations between the lower flammability limit and the upper flammability limit. The lower flammability limit is the minimum concentration of hydrocarbon vapor or gas in air or oxygen-enriched air below which flame propagation does not occur on contact with a source of ignition; the upper flammability limit is the maximum concentration of hydrocarbon vapor or gas in air or oxygen-enriched air above which flame propagation does not occur on contact with a source of ignition. Fires and explosions can be prevented by operating outside of the flammability range. The lower flammability limit of hydrocarbons in air at STP is generally in the range of 1 to 5 mol %, and it remains nearly independent of oxygen composition because it is fuel-limited. The upper flammability limit of hydrocarbons in air at STP varies from roughly 10 to 20 mol %. As the oxygen mole fraction increases above the 0.21 level of air, the upper flammability limit of hydrocarbons increases as (Bodurtha, 1980):

$$\Delta U_c \simeq 70.0[\log(y_{O_2}) + 0.678] \tag{10}$$

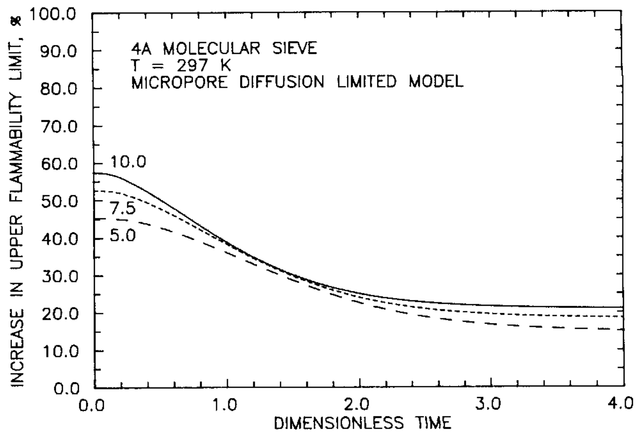

Figure 7. Predicted increase in the upper flammability limit of a hydrocarbon fuel in contact with the effluent gas emerging from a thermally regenerated air drier containing 4A molecular sieve.

The increase in the upper flammability limit is relative to that in air at STP. The dimensionless time equals the number of bed volumes of gas which have passed through the adsorber, based on an empty vessel.

Elevated pressures also widen the flammability range. While the lower flammability limit of hydrocarbons decreases very slightly with increasing pressure, the increase in the upper flammability limit of hydrocarbons increases in proportion to the logarithm of the total pressure (Bodurtha, 1980):

$$\Delta U_p \simeq [20.6 \log(P) - 5.00] \tag{11}$$

The composition and pressure effects (Eqs. 10 and 11, respectively) can be summed to find the total increase in the upper flammability limit of hydrocarbons:

$$\Delta U = \Delta U_c + \Delta U_p \tag{12}$$

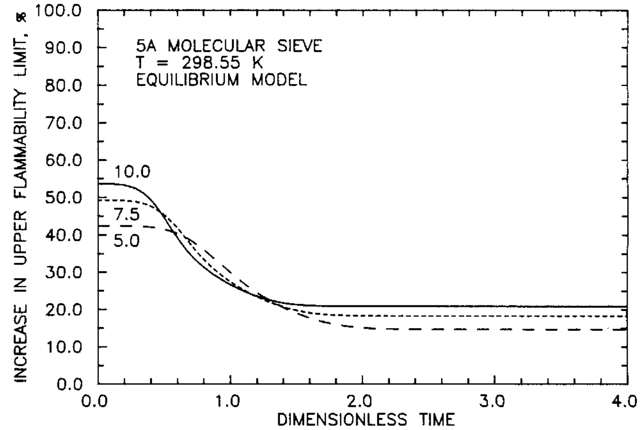

Figure 8. Predicted increase in the upper flammability limit of a hydrocarbon fuel in contact with the effluent gas emerging from a thermally regenerated air drier containing 5A molecular sieve.

The increase in the upper flammability limit is relative to that in air at STP. The dimensionless time equals the number of bed volumes of gas which have passed through the adsorber, based on an empty vessel.

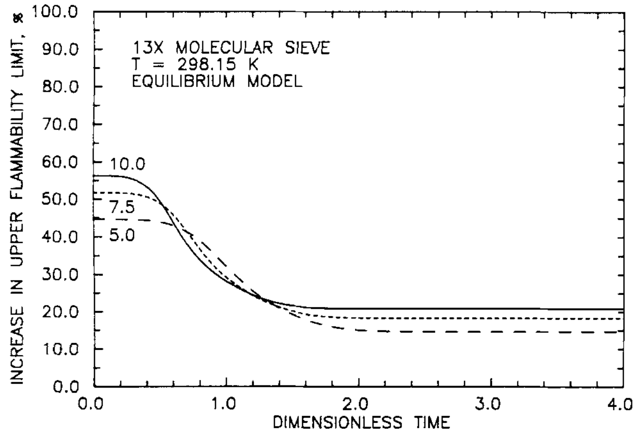

Figure 9. Predicted increase in the upper flammability limit of a hydrocarbon fuel in contact with the effluent gas emerging from a thermally regenerated air drier containing 13X molecular sieve.

The increase in the upper flammability limit is relative to that in air at STP. The dimensionless time equals the number of bed volumes of gas which have passed through the adsorber, based on an empty vessel.

Figures 7, 8 and 9 show the total increase in the upper flammability limit of hydrocarbons as oxygen-enriched effluent emerges from thermally regenerated air driers containing 4A, 5A and 13X molecular sieves, respectively. These results were obtained by applying Eq. 10 through 12 to the results illustrated in Figures 4 through 6. The dimensionless time of zero corresponds to the instant the adsorber vessel is brought on-line. Here, both the composition and total pressure effects lead to an increase in the upper flammability limit of approximately 50 mol %. At a dimensionless time of 4, oxygen-enriched effluent no longer emerges from the adsorber. Then, the upper flammability limit increases by 15 to 20 mol % because of the pressure contribution only.

Increases in both the total pressure and the oxygen mole fraction decrease the minimum autoignition temperature of hydrocarbons relative to air at STP. The minimum auto ignition temperature is a measure of the thermal energy required to initiate combustion; specifically, it is the lowest temperature at which the fuel spontaneously ignites. Table 3 indicates that the minimum auto ignition temperatures of kerosene and mineral oils fall to roughly 500 K at a total air pressure of 10 atm (Kuchta et al., 1962; Zabetakis et al., 1962; McCoy and Hanly, 1975).

Table 3. Minimum Autoignition Temperatures of Hydrocarbon Fuels (K)[‡]

Pres. (atm)	Kerosene[*]	Type of Hydrocarbon Fuel Mineral Oils[**]	Mineral Oils[†]
0.25	866	---	---
0.50	737	---	---
1.0	502	623	568
10.0	---	523	535
100.0	---	473	502

[*] From Kuchta et al. (1962).
[**] From Zabetakis et al. (1962).
[†] From McCoy and Hanly (1975).
[‡] Normal hexane and longer normal paraffins have auto ignition temperatures of 480 to 500 K in air at STP (Bodurtha, 1980).

An increase in the oxygen composition also decreases the minimum auto ignition temperature. For example, Kuchta et al. (1965) found that the minimum auto ignition temperature of a kerosene fuel (JP-6) at 1 atm decreased by 0.16 K for each percent increase in the oxygen mole fraction.

The presence of iron oxides (rust) catalyzes the oxidation of oil and coke deposits, and lowers the minimum auto ignition temperature of oils by roughly 50 K (Hilado and Clark, 1972; McCoy and Hanly, 1975). Other metal oxides can also promote oxidation and lower the minimum auto ignition temperature of hydrocarbons (Bodurtha, 1980).

Increasing the total pressure and oxygen mole fraction above that of air at 1 atm leads to a higher ultimate explosion pressure (Bodurtha, 1980). The pressure contribution follows from the ideal gas law, where the final pressure in a closed system increases in proportion to the initial pressure, the ratio of final to initial moles of gas, and the ratio of final to initial temperatures:

$$P_2 = \frac{P_1 n_2 T_2}{n_1 T_1} \tag{13}$$

An increase in the oxygen mole fraction will raise the ultimate explosion pressure if it allows more fuel to react. Combustion of a volatile liquid or solid increases the ultimate explosion pressure relative to a flammable gas since combustion of a volatile liquid or solid produces a larger change in the ratio of moles of gas.

Additionally, increasing the total pressure and oxygen mole fraction above that of air at 1 atm typically produces a higher combustion rate, which forces the explosion pressure to rise more rapidly and increases the severity of an explosion (Cousins and Cotton, 1951; Nagy et al., 1971). Although combustion kinetics can be very complex, combustion rates typically accelerate with increasing fuel and oxygen partial pressures.

Problems in process equipment

Process equipment can provide sources of hydrocarbons and sources of ignition. Compressors which follow air driers provide both sources and complete the "combustion triangle." Auto ignition and detonation of compressor lubricating oils due to an increased oxygen concentration in the compressor inlet gases have been reported frequently (Rendos, 1963; Rogers and Wilson, 1965; Ball and Kitson, 1965).

Fire and explosion hazards are greatest in reciprocating compressors (Rekstad, 1965; Burgoyne and Craven, 1973). The tendency to overlubricate compressors contributes to the fuel source problem and permits unnecessary quantities of oil to be carried downstream. Explosions have started in centrifugal compressors as well (Gibbs, 1960; Rekstad, 1965). They have a smaller chance of exploding because the lubricants enter a centrifugal compressor case only if the seals leak.

Pipelines coated with oil on their interior and charged with air present a severe explosion hazard (Loison, 1952; Reed, 1939). Intermittent flow, especially a sudden start of air flow, facilitates the ignition of oil residues by depressing the autoignition temperature to 425 K (Loison, 1952). Similarly, a rapid pressure increase of 100 psi (689 kPa) ignited oil contaminated with rust at temperatures of roughly 400 K (Faeth and White, 1961). When a thermally regenerated air drier which contains large pore molecular sieves is brought on-line, the sudden start of flow of effluent gas with a high oxygen partial pressure greatly exacerbates the risk of fires and explosions. Fires have been reported to occur in pipelines downstream of instrument air driers (Huff and Craven, 1973), but this is the first article to attribute these incidents to oxygen enrichment and the choice of adsorbent.

Electrostatic sparks provide a source of ignition in many kinds of chemical process equipment. Hearn (1991) claims that the electrostatic spark from an isolated, ungrounded process or the electrostatic discharge from (adsorbent) pellets in large vessels can supply ample energy to ignite fuels such as hydrocarbons, polymers (coke deposits), and powders.

Remedies

A variety of strategies might be employed to minimize oxygen enrichment and the hazards it presents in and downstream of thermally regenerated air driers which contain large pore molecular sieves. One could eliminate the hydrocarbons and sources of ignition, but this is easier said than done and beyond the scope of this article. Here, we discuss air drying process modifications which can minimize or prevent transient oxygen enrichment.

Thermally regenerated air driers are generally installed in pairs so that one adsorber is on-line while the other is reactivated. Reactivation involves a series of steps, usually sequenced as follows: depressure, heat adsorbent, cool adsorbent, and repressure. To reduce oxygen enrichment downstream of the adsorbers, one could bleed effluent from the adsorber being repressured into the process stream exiting the other on-line adsorber. This adjustment requires extra operator attention and only attenuates the oxygen enrichment. Short-term venting of the effluent could eliminate downstream problems but would not eliminate the enrichment problem within the adsorber vessels.

Alternatively, one could install a large surge tank downstream of the adsorber to dilute the oxygen enrichment. This scheme requires additional capital and plot space unless a surge tank is already in place. If a surge tank is located between a compressor and the adsorber, it may be possible to repipe the process so that the surge tank follows the adsorber rather than the compressor. Unfortunately, placing an adsorber downstream of a reciprocating compressor may agitate the adsorbent particles, causing them to crumble and thus raising the pressure drop across the adsorber. With a reciprocating compressor two surge tanks would be required: one after the compressor to dampen fluctuations in the flow rate and one after the air drier to dilute the transient oxygen enrichment.

One could also operate the adsorbent heating and cooling steps at the same pressure as the adsorption step, thereby eliminating the need to depressure and repressure the adsorber. Some oxygen enrichment may still occur as air contacts the activated molecular sieve at the beginning of the adsorption step, however. Eliminating the repressure step may not be feasible given the source and pressure of some regeneration gases. Isobaric operation also curtails the useful cyclic capacity of the adsorber because the thermal regeneration step operates less efficiently at higher pressures. Lastly, one would still need to repressure the air drier during the initial startup and during subsequent startups following every shutdown.

Basmadjian (1975) has provided criteria which indicate that the cooling step may be omitted without hindering water removal during the subsequent adsorption step. Omitting the cooling step would also dilute and extend the oxygen enrichment over the time required for the molecular sieve to cool during the subsequent adsorption step. Hot effluent air may not be acceptable in processes such as life support systems, wind tunnels, dry atmospheres for packaging and storage of biological materials, and cryogenic processes. Without a cooling step the adsorber effluent gas temperature may be above the auto ignition temperature of hydrocarbons in air, in which case one has substituted the hazards associated with high temperature for the hazards associated with oxygen enrichment. Passing air at high pressure through a hot adsorber containing coked adsorbent may ignite the coke and possibly cause a runaway combustion reaction in the adsorber.

Rather than modify the operation of thermally regenerated air driers, one could substitute an adsorbent which does not adsorb nitrogen to the same extent as 4A, 5A or 13X molecular sieve. We recommend 3A (K-A) molecular sieve, which adsorbs no oxygen or nitrogen because the 3A micropores are too small to admit oxygen and nitrogen. Using 3A molecular sieve provides a simple, safe and inexpensive way to eliminate transient oxygen enrichment.

Type 3A molecular sieve is clearly the adsorbent of choice for air drying applications. Other possible adsorbents for drying air include activated alumina and silica gel, but these materials have several disadvantages relative to 3A molecular sieve. Both activated alumina and silica gel have a lower affinity for water than types A and X molecular sieves (Ruthven, 1984; Wankat, 1986; Yang, 1987). Activated alumina and silica gel cannot attain the low dewpoint temperatures characteristic of types A and X molecular sieves.

Activated alumina and silica gel pose a greater safety threat than does 3A molecular sieve because they acquire coke deposits which act as a fuel and as an adsorbent. Activated alumina and silica gel readily adsorb hydrocarbons (Ruthven, 1984; Wankat, 1986; Yang, 1987), some of which react to form coke on these adsorbents. Compressor lubricants are a common source of hydrocarbons; varying amounts of hydrocarbons present in ambient air are another possible problem. Because only low molecular weight hydrocarbons desorb during the reactivation steps, activated alumina and silica gel can accumulate sufficient hydrocarbons or coke deposits to cover nearly 100% of their surface area. The resulting hydrocarbon film or coke layer of several hundred square meters per gram of adsorbent is an abundant quantity of accessible fuel. In comparison, hydrocarbons can enter only the macropores in the clay binder of 3A molecular sieve; all hydrocarbons are too large to penetrate the 3-Å apertures to the interior cavities. The macropores of the clay binder comprise only about 1% of the total surface area of type 3A molecular sieve, amounting to less than 5 m^2/g of adsorbent. Thus, use of 3A molecular sieve effectively minimizes hydrocarbon and coke deposits as a fuel.

Coke deposits covering a significant fraction of the surface area of the myriad pores of activated alumina and silica gel may become an important secondary adsorbent. Specifically, coke deposits in activated alumina and silica gel may behave like activated carbons which adsorb oxygen, sometimes preferentially relative to nitrogen (Deitz, 1944; Maslan et al., 1953; Knoblauch, 1978; Ruthven et al., 1986). Oxygen adsorbed on carbon has long been known to present a grave risk of fire and explosion, even at liquid air temperatures (less than 100 K) (Deitz, 1944). Fire and explosion hazards involving coke deposits which adsorb oxygen preferentially relative to nitrogen could be severe, primarily because large quantities of molecular oxygen intimately contact the coke. For those coke deposits which adsorb nitrogen preferentially relative to oxygen, the oxygen-enriched gas will present fire and explosion hazards downstream of the adsorber as well.

At present, we are not aware of any quantitative data to support the notion that coke deposits can behave like activated carbons and adsorb nitrogen and oxygen. It, however, provides the best explanation for several instances where fires have started in air driers when coke and hydrocarbons in the pores of activated alumina and silica gel ignited during the repressurization and adsorption steps. In all of these instances, the fires damaged the adsorber vessel and sometimes nearby process equipment too. Thus, operating precedents strongly suggest that activated alumina and silica gel pose safety threats that 3A molecular sieve eliminates.

If type 3A molecular sieve has been installed in thermally regenerated air driers, it has been for reasons other than to prevent oxygen enrichment and the deleterious effects it can cause. For example, 3A molecular sieve may have been the only adsorbent available when another spent adsorbent was replaced. At present, drying of reactive hydrocarbons constitutes the only intentional use of 3A molecular sieve in regenerative adsorption applications (Pierce and Stieghan, 1966).

Conclusions

Simulations were used to quantify the performance of thermally regenerated air driers which contain 4A, 5A or 13X molecular sieve. The results demonstrate that nitrogen adsorbs preferentially relative to oxygen in 4A, 5A and 13X molecular sieves during the repressurization step and that oxygen-enriched effluent at high pressure emerges when an adsorber is brought on-line.

The high gas-phase oxygen concentration expands the flammability range of hydrocarbons, markedly lowers the minimum auto ignition temperature of hydrocarbons, and produces both a higher explosion pressure and a higher rate of explosion pressure rise compared with air at standard temperature and pressure. Fuel and ignition sources may be found in compressors, pipelines with an oil film on the inside walls, and coke deposits on adsorbents, for example. Consequently, oxygen-enriched gases pose severe fire and explosion hazards in and downstream of thermally regenerated air driers which contain 4A, 5A or 13X molecular sieve. Substituting 3A molecular sieve for the commonly used 4A, 5A and 13X molecular sieves provides a simple, safe and inexpensive way to prevent transient oxygen enrichment and the deleterious effects it can cause.

Activated alumina and silica gel can be substituted for types 4A, 5A and 13X molecular sieves, but they have several disadvantages relative to 3A molecular sieve. Activated alumina and silica gel cannot dry air to the low dewpoint temperatures characteristic of types A and X molecular sieves. Hydrocarbon and coke deposits, which may cover nearly the entire surface of activated alumina and silica gel, provide a plentiful source of fuel. Coke deposits may also acquire the adsorption characteristics of activated carbon, which would exacerbate the combustion problem and possibly lead to transient oxygen enrichment. In contrast, 3A molecular sieve can accumulate hydrocarbons and coke deposits on only about 1% of its surface area, which virtually eliminates coke deposits as fuel and as an adsorbent. Type 3A molecular sieve is clearly the adsorbent of choice for air drying applications.

Patents have been applied for based on the technology described herein.

Notation

a_i = parameter in Langmuir adsorption isotherm for species i, mol i/kg adsorbent/(N/m^2)
b_i = parameter in Langmuir adsorption isotherm for species i, m^2/N
c_i = gas-phase concentration of species i, mol/m^3
$D_{M,i}$ = effective diffusivity of species i in macropores, m^2/s
$D_{m,i}$ = diffusivity of species i in micropores, m^2/s
L = length of adsorbent bed, m
n = quantity of gas phase molecules, mol
P = total pressure, N/m^2
q_i = concentration of adsorbate i on the adsorbent, mol/kg
q^*_i = equilibrium concentration of adsorbate i on the adsorbent, mol/kg
r = molecular sieve pellet radius, m
r_z = zeolite crystal radius, m
R = gas constant = 8.314 J/mol/K
t = time, s
T = absolute temperature, K
u = interstitial velocity, m/s
u_o = ϵu = superficial gas velocity, m/s
U = upper flammability limit of hydrocarbon, mol %
y_i = mole fraction of species i
z = axial position in the adsorbent bed, m

Greek letters

Δ = change in parameter which immediately follows
ϵ = interparticle void fraction
ρ_b = bulk density of the adsorbent, kg/m^3
$\tau_{M,i}$ = time scale for macropore diffusion for species i, s
$\tau_{m,i}$ = time scale for micropore diffusion for species i, s

Subscripts

c = due to oxygen concentration increase
i = species label
j = species label for summation
n = number of species
p = due to total pressure increase
1 = initial conditions
2 = final conditions

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Manuscript received June 6, 1991, and revision received May 29, 1992.