Gas Centrifugation with Wall Condensation

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Introduction

Current large throughput gas cleaning processes are not able to deal with highly contaminated gas fields. Amine treatment is typically used for removing these contaminants — CO_2 and H_2S — from gas, but is not economic or practicable for highly contaminated gas, that is, where the concentrations of CO_2 or H_2S are above ca. 10 and 5%, respectively.[1,2] Another major disadvantage is the low pressure at which waste gas is produced — compression is then required for waste disposal processes, such as reinjection.

An alternative candidate process which has recently been evaluated is centrifugal gas separation.[3] A gas centrifuge is basically a cylinder, filled with a gas mixture, and rotating at high speed. Due to the large centrifugal forces, the gas is pushed to the wall, resulting in a pressure gradient. Gases with different molecular weights have different partial pressure profiles and their mole fraction profiles vary with radius. In a methane/carbon dioxide mixture, the concentration of the CO_2 increases near the wall by diffusion along the concentration gradient. We have shown experimentally that a purely gaseous process is too slow for practical application.

Increasing the pressure is not that helpful for component separation in the gas phase, because to a first approximation the product of diffusion constant and pressure pD is constant that is, at high pressures the diffusion constant decreases.[4] However, at the higher pressures generated in a centrifuge, there is a second much more dominant mechanism which will also cause separation — namely condensation due to the radial compression.[5] This effect has some similar physical properties to what happens in the so-called evaporative centrifuge which has been previously analyzed for isotope separation, and which we have recently shown to be quite different from natural gas separation behavior in a centrifuge.[6]

In this study we examine whether condensation speeds up the separation process for a contaminated natural gas scenario. We identify two mechanisms for this condensation. A model is constructed which simulates the effect of condensation by centrifugal enrichment. The results of this model are compared to results of simulations of a gas/gas centrifuge. It is investigated in how far the concept of wall condensation leads to a significant increase of the separator performance in comparison with that of pure gas/gas separation by centrifugation.

Theory and Model

Figure 1 shows the condensation curves at different temperatures for various mixtures of methane/CO_2 as a function of the concentration of CO_2 in the mixture. This was calculated using an extended equation of state program based on a cubic equation of state of the Soave-Redlich-Kwong type. There are, in the case of a condensing centrifuge, two mechanisms for condensation. Pure *compression* work corresponds to moving up the vertical pressure line: for example, with a 50/50 CO_2/CH_4 mixture at -25 °C, if we increase the pressure (for example, along the radius of the centrifuge rotor) then around 40 bar, condensation of a CO_2 rich waste liquid starts to occur. Pure *enrichment* work corresponds to moving horizontally to the right whereby the local concentration of CO_2 at any point is increased as a result of centrifugally induced diffusion. For example, if we started with a 25 bar 50/50 mixture of CO_2/CH_4 and allowed CO_2 enrichment to proceed near the rotor wall, then around $x_d = 0.6$, condensation will occur.

Thus, rather than considering Figure 1 to be a curve which shows condensation pressure p_d as a function of composition x,

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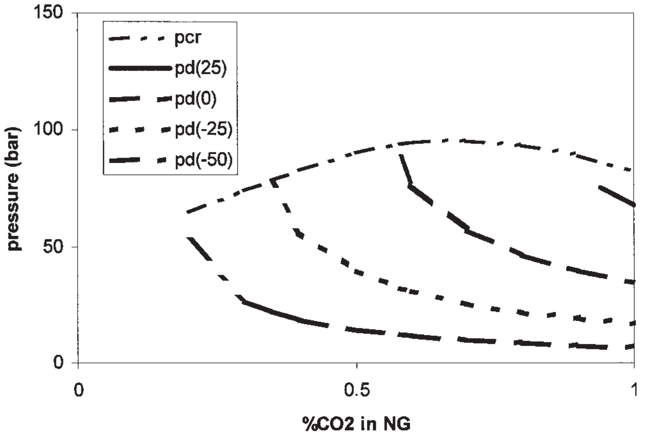

Figure 1. Condensation curves at different temperatures as a function of %CO_2 in natural gas.

Thus, pd(T) refers (for temperature T) to the pressure at which the first condensed liquid forms (also known as the "dewpoint"). The envelope gives the critical pressure denoted "pcr".

we may equally well consider it as a curve which shows the condensing composition x_d as a function of pressure p. It is with this latter function which we are concerned, and which forms the focus of our effort to see to what extent condensation enhances centrifuge performance above pure gas/gas operation. We want to resolve and extrapolate pure compression and pure centrifugal enrichment contributions to separation.

The core idea in this work is, thus, to operate the centrifuge with a sufficiently high-feed pressure that when the gas mixture is spinning, then at a certain radius, condensation will occur. This idea is shown in Figure 2. Initially the process runs identically to the gas-gas centrifuge. However, at one point along the radius, at $r = r_d$, the pressure is sufficient that the condensing pressure is reached. Initially, when the pressure profile is (almost instantaneously) established, we still have a uniform composition throughout the cylinder, because the diffusion process concentrating CO_2 near the wall occurs more slowly than the fast pressure generation profile — at this point r_d is determined purely by the partial pressure. Subsequently, centrifugally driven mass transfer occurs of CO_2 from the center to the outer region of the centrifuge. This net transport of CO_2 has the effect of shifting condensation closer to the center to the equilibrium value.

The region where condensation occurs is shown in Figure 2 by the shaded area, where the pressure exceeds that required for condensation of liquid (referred to as the "dewpoint"). The condensing separation is faster than pure gas-phase separation because CO_2 is removed from the gas phase. This will act to further drive the mass transport of CO_2 from the center to the outer radial annulus.

In our analysis of the condensing centrifuge we have followed the techniques and criteria which we have previously derived[4]. Since the fundamental concern is to determine whether the condensation will help speed up the centrifugal process, we perform our calculation with respect to the batch process in order to determine the reduction in separation time due to condensation. The unit is filled with gas to a feed pressure just below the condensation pressure for the mixture (in this case 50/50 CH_4/CO_2). The mixture is then spun-up and instantaneously acquires the centrifugal pressure profile with uniform feed composition. There is, thus, a portion of radially uniform concentration gas near the wall which is at a pressure above the condensation pressure. Condensation of CO_2 rich liquid occurs rapidly and is considered removed from the system. However, this has the effect of changing the total composition of the remaining gas phase and reducing the total number of gas molecules thus leading to an overall pressure reduction so that condensation stops. The remaining gas now undergoes a much slower centrifugal enrichment process to a new radial composition distribution. The composition distribution is enriched in CO_2 near the wall so that the local condensing pressure is exceeded and the process iteratively cycles until no more condensation occurs.

In a gas centrifuge, the dimensionless partial differential equation describing the time-dependent mole fraction distribution of one component is.[6,7]

$$\frac{\rho r_0^2}{\rho D}\frac{\partial x_1}{\partial t} = \frac{1}{r^*}\frac{\partial}{\partial r^*}\left(r^*\frac{\partial x_1}{\partial r^*} + 2(A_2 - A_1)x_1(1 - x_1)(r_0 r^*)\right)^2 \tag{1}$$

where D is the diffusion coefficient (m^2/s), ρ the mixture mass density ($kmol/m^3$), r_0 the wall radius, r^* the dimensionless radial coordinate, defined as $r^* = r/r_0$, t denotes time (s), x_i the mole fraction of component i. Whereas for a centrifuge where only gas-gas separation occurs, the boundary conditions are constant, in a condensing centrifuge these vary continually and are a function of composition. Condensation occurs, resulting in liquid, which because of its higher density and the large centrifugal forces, is pushed to the wall, where it is extracted. This removal of mass from the system results in new boundary conditions — those for the gas/gas case are no longer valid. The feed concentration is equal to the condensation concentration for the wall pressure at $t = 0$

$$x_{Feed}(r^*, t = 0) = x_{Dewpoint}(p_{wall}(t = 0)) \tag{2}$$

Any liquid that is formed by condensation is considered to be removed instantaneously. Since this will only occur at the wall, it is sufficient to correct the boundary conditions at the wall

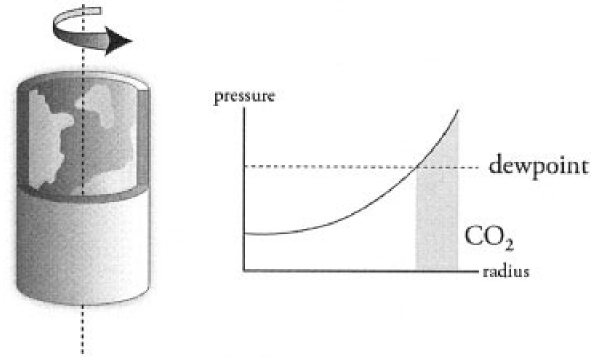

Figure 2. Principle of operation for condensing centrifuge.

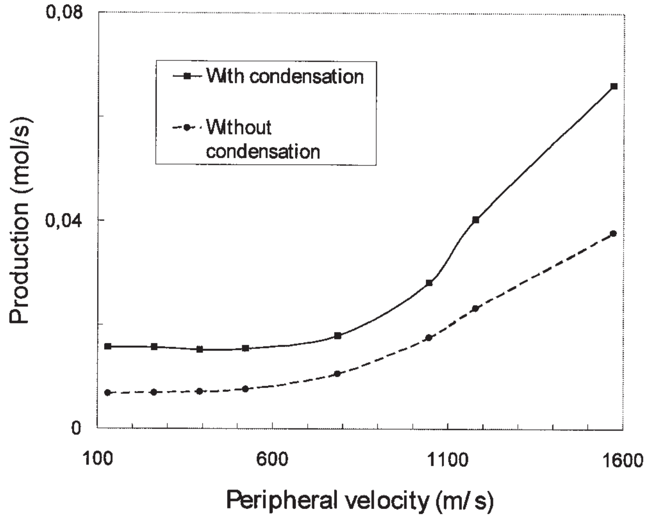

Figure 3. Production as a function of peripheral velocity for enrichment levels equal to that of the gas/gas centrifuge.

$$\text{if } p_{wall} \geq p_{sat} \text{ then } x(r_0 t) = x_{Dewpoint}(p_{wall}(t)), \quad \text{for } 0 < z^* < 1 \tag{3}$$

Equation 1 is solved using the finite volume method in Aspen Custom Modeler® (ACM — an equation oriented modeling package), and the boundary conditions discussed earlier. The problem is set up as spatially axisymetrically discretised along a uniform grid and time integration is performed with a fourth order Runge-Kutta algorithm. Peripheral velocity and centrifuge length are the only two independent design variables; this can be seen in Eq. 1 which is dependent on the peripheral velocity. Radial velocity and wall radius are, therefore, not independent parameters. The centrifuge has a length of 1 m. All condensed liquid is considered to be removed instantaneously. The remaining gas is considered to be the product gas. Product flow is calculated by dividing the gas mass by the time required to perform the separation. Since product flow and product enrichment, that is, product composition, are not independent variables, the product flow is calculated as a function of the enrichment level that the gas/gas centrifuge would have at the given peripheral velocity. It has been previously shown that one cannot[5,6] realistically use the steady-state enrichment level of the noncondensing gas-gas centrifuge, as this would take infinitely long to achieve, but an enrichment level that is 90% of this steady-state enrichment. The time t_{90}, to reach this 90% of equilibrium enrichment, is used to calculate the product flows of the noncondensing gas-gas centrifuge. This enables us to compare the performance of the condensing centrifuge with the noncondensing, purely gas phase centrifuge.

Results and Discussion

Figure 3 shows that condensation processes yield a product flow that is approximately twice that of the gas/gas centrifuge. The doubling of the removal rate due to condensation of a centrifugally enriched mixture is still small compared to the pure compression work which removes a large amount of the CO_2. Note that we are here focussing on the removal due to enrichment work decreasing the condensation pressure, that is, we have specifically excluded the compression work. Independent of inlet conditions, we first remove all condensed material assuming rapid phase separation under the imposed pressure gradient. If, however, the compression removal is included then of course a much higher throughput can be obtained — however a gas centrifuge is not the ideal way for carrying out compression — although it does have the advantage of a predetermined spatial separation of gas and liquid phase inside the rotor, as opposed to the spatially uniform behavior in a compressor. In any case, for pure centrifugal condensation, the rate is still dependent on the CO_2 molecules diffusing to the wall where they concentrate sufficiently to decrease the local condensing pressure below the local quasi-stationary pressure. The process, thus, still depends on diffusion, but over a smaller distance.

This model has used a batch centrifuge to calculate the time required for separation. It has previously been shown that the countercurrent continuous process is faster than the batch version by a factor of 2 – 5 depending on operating conditions – however, this augmentation in process rate is certainly not by the order of magnitude, which we require for commercial utilisation. It is, thus, unfortunately clear, that a countercurrent condensing centrifuge will not enable sufficiently fast separation to be of commercial interest. Although there is some improvement, product flows are still of the same order of magnitude. Our own experiments[8] indicate that an improvement of several orders of magnitude is required to make gas/gas centrifugation a viable option for removing contaminating gases from natural gas streams. Condensation by compression has more potential, since it is not a diffusion dominated process. However, since the gas centrifuge is not a dedicated compression device, and the benefits of the centrifugal enrichment are limited, it is better to seek for other means to optimize this process.

In the centrifugation process described here, two separate unit operations (that is, compression and separation) were combined. We are currently experimentally developing these processes in a line-up where the operations are separated out, that is, sequential condensation and centrifugal separation. We have previously shown that for high axial throughputs, the rotor bowl needs to contain a permeable medium.[9] This is a requirement for suppressing turbulence generally, and also for decoupling the high axial turbulence associated with large throughputs from the radial flow under centrifugation — the latter has to be kept laminar. In the case of a medium containing condensed waste liquid to be separated out, then a structured medium containing radial and not just axial permeability with gas porous walls (such as a channelled monolith) would be required. This is in fact, the same as using a mist mat — known in technology applications for removing condensate from gas streams. The difference is that it would actually form the rotating element in the centrifugal separator. Such considerations, along with the times to develop separable size condensing nucleii are the focus of our current studies.

Finally, it is worth drawing attention to one interesting result. The major application of centrifuges to date has been for separating out isotopes of UF_6. In that process, low-pressure (and, thus, low throughput) operation is required in order to avoid reaching the desublimation pressures of UF_6 (0.16 bar at 20°C) which unbalance the spinning cylinders due to assymmetric solids formation on the walls. This is not a problem if liquids could be formed as they will spread symmetrically around the rotor circumference. This would require operation between the triple point of UF_6 (64°C, 1 bar) and the critical point of that material (233°C, 47 bar). In that regime a liquid/gas boundary can be formed for condensation in the scheme we have identified earlier. We wonder whether the process we have described in this study has ever been considered for uranium enrichment — normally, higher temperatures are avoided because the equilibrium separation is less favorable — however, in this case there is a clear processing advantage. The higher production rates here are still of interest because of the higher unit value of the enriched isotope compared to natural gas.

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