



Landfill Gas: From Rubbish to Resource

KENT S. KNAEBEL AND HERBERT E. REINHOLD
Adsorption Research Inc., Dublin, OH 43016-1200, USA

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Abstract. The prospects of using landfill gas (LFG) as a high-grade fuel in the immediate future, in view of environmental regulations, the *Kyoto Protocols*, and energy prices, are discussed. Adsorption cycles suggested in the late 1980s by Sircar and co-workers for treating LFG are reviewed: one produced CO₂-free methane and the other produced both CO₂-free methane and methane-free CO₂. Neither of those could be used to produce pipeline quality gas from LFG, due to contaminants such as nitrogen. Two new three-stage flowsheets are discussed as a means to separate pipeline-grade methane from LFG. One is a hybrid membrane—PSA system. The other is a TSA—PSA system. The third stage of both of these systems is crucial to obtaining pipeline quality gas, i.e., a PSA unit to extract the nitrogen and other light gases from methane. A novel PSA cycle is suggested and explained in terms of: a model by which the recovery, power requirements, and adsorbent bed size can be estimated.

Keywords: pressure swing adsorption, purification, bulk separation, environmental application

Introduction

Municipal waste is delivered to landfills, then the waste is generally spread out, compacted, and covered with a fresh layer of soil each day. Waste deposited in landfills decomposes by microbial action to form methane, carbon dioxide, and water. The gaseous product, called landfill gas (LFG), contains dozens, if not hundreds, of miscellaneous contaminants, such as volatile organic compounds (VOCs), e.g., vinyl chloride and methylene chloride, as well as hydrogen sulfide, siloxanes, freons, etc. LFG is called a biofuel, since plant material (biomass) is a significant component of municipal solid waste. In that vein, it is viewed as a renewable resource.

Methane is obviously the most valuable component in LFG, but it is also potentially harmful, in that its so-called greenhouse potential is about $21 \times$ that of carbon dioxide. Nitrogen, and oxygen to a much less extent, may appear in LFG if the gas is collected at pressures well below atmospheric. That mode of operation is necessary to achieve high yield, but unavoidably mixes air with LFG. The air is depleted in oxygen due to

microbial action, which is at least partly aerobic near the surface.

The simplest disposal option, combustion without prior enrichment, diminishes the potential greenhouse gas effect of CH₄ in LFG. To minimize capital investment, it may be burned in a flare. Alternatively, it may be converted to a useful form of energy in a boiler to generate steam, or in a motor. Depending on the analysis of the LFG, the latter options may be precluded or may be much more expensive than envisioned. That is because, if the LFG contains chlorinated VOCs (e.g., vinyl chloride) or silicon-bearing components (e.g., siloxanes), corrosion or silicon oxide deposits may require premature and costly overhauls. In such cases, it is necessary to purify the gas, to remove destructive compounds, prior to extracting the energy.

Besides combustion without prior enrichment, LFG can be upgraded to produce high quality fuel. That requires removing most if not all of the CO₂, moisture, and N₂, in addition to the contaminants mentioned above. Adsorption, membranes, or cryogenic distillation can be used to improve the heating content or fuel value of LFG. Then it may be distributed in a pipeline or

at filling stations for vehicles. Membranes may be useful for splitting CO_2 and moisture from LFG, though there are inherent losses of CH_4 due to modest selectivity. Cryogenic distillation would only be feasible in very large applications, probably beyond the capacity of most landfills at present. In contrast, pressure swing adsorption (PSA) and temperature swing adsorption (TSA) can also separate those components, as well as N_2 , and can operate with high recovery.

Previous studies were conducted by Sircar (1988) and co-workers (1988). Those studies addressed many of the major issues, and led to commercial endeavors at several sites. The commercial product line of Air Products was referred to as the Gemini 5 System. The objective of that work was to split a mixture containing CH_4 and 40 to 60% CO_2 , and to obtain high Btu gas for combustion and, optionally, purified CO_2 for industrial applications.

Sircar's two embodiments are shown schematically in Figs. 1 and 2. The first only produces CH_4 , and the second produces both CH_4 and CO_2 . Comparisons were based on 13X zeolite adsorbent and a feed containing 57% CH_4 , with a pressure swing of about 0.12 to 4.8 bar (or a pressure ratio of 40). The first used less power (by 40%) for evacuation but consumes N_2 as a purge gas. During blowdown and evacuation, the second produced 99% CO_2 , and 99% CH_4 during the feed step. The corresponding recoveries were about 98% and 99%, respectively.

In the above cited patent, Sircar and co-workers mentioned that landfill gas contains many impurities, including hydrocarbons (aliphatics and aromatics), and chlorinated organic solvents. Many of those would reduce the working capacity of the PSA adsorbent, by adsorbing much more strongly than CO_2 . In fact, they recommend a pretreatment section comprised of a TSA unit, which employed activated carbon mostly and some 13X zeolite, and a thermal swing of more than 400°C .

Current Trends

The world today has changed significantly since the late 1980s. Even in the U.S., there have been dramatic changes. At that time energy prices were fairly stable, while over the past year we have seen a 5-fold increase and subsequent decline in the price of domestic natural gas. In the 1980s destruction of the ozone layer was viewed as a significant environmental problem, while today we are more focused on global warming, viz. the *Kyoto Protocols on Global Climate Change*. Taxes were being cut in the 1980s, while today our government is contemplating a tax of \$50 per ton of carbon consumed.

As a possible harbinger of what is to come, the State of Massachusetts recently enacted legislation to: reduce by 10% the allowable CO_2 emissions per MW·hr (i.e., to 818 kg/MW·hr). This means that a typical power

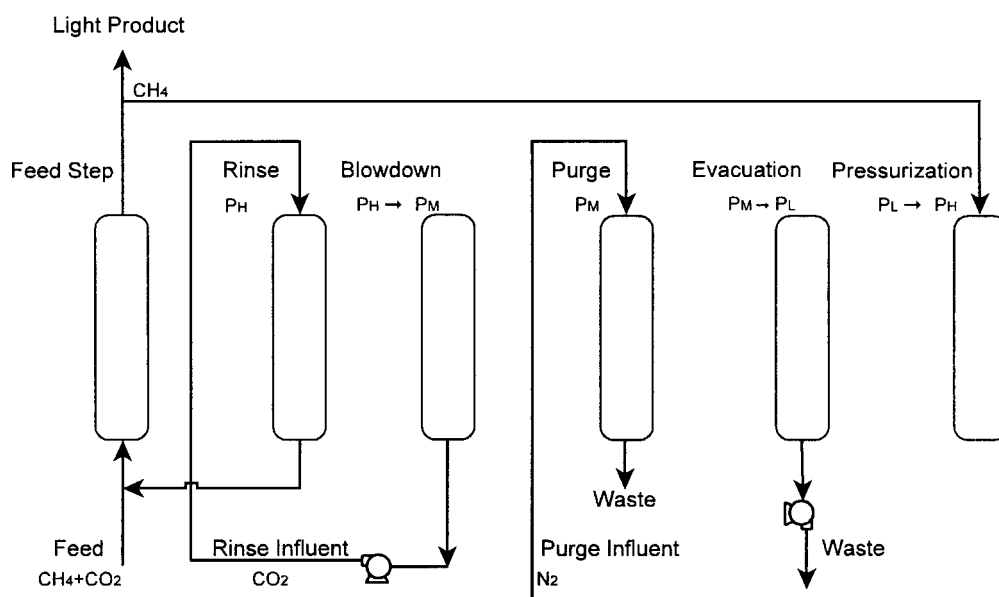


Figure 1. Schematic diagram of Sircar's six-step cycle for CH_4 production.

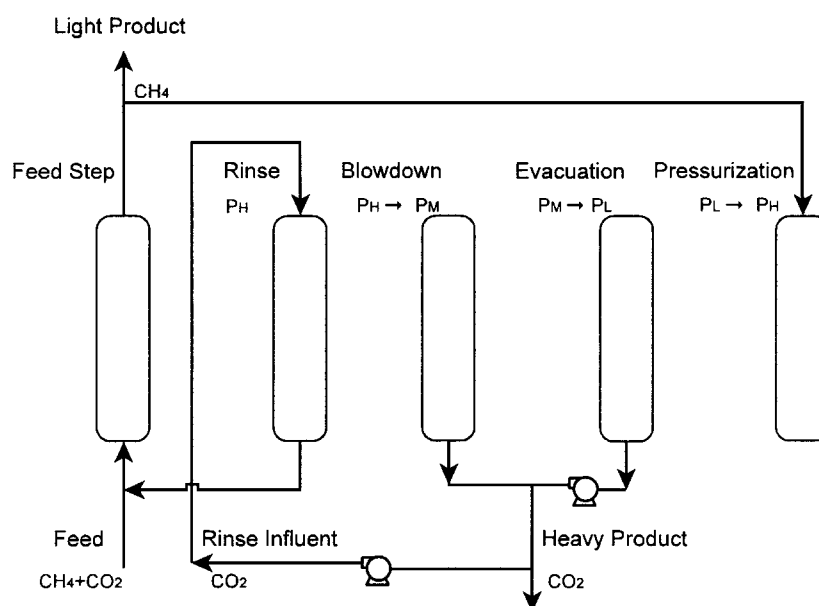


Figure 2. Schematic diagram of Sircar's five-step cycle for CH_4 and CO_2 production.

plant must achieve an approximate efficiency of 39.5%, which is close to the state-of-the-art. Compliance is required by 2008. Potential remedies are improved efficiency, trading CO_2 credits, or sequestration. To compensate for an older, less efficient power plant which might emit 1,000 kg/MW·hr, it would be necessary to achieve a reduction to 641 kg/MW·hr in a new plant. To accomplish that would require achieving an efficiency of 50%, which is not economically practical. Thus, Massachusetts has effectively legislated the closure of older power plants.

Global warming is still controversial, but there are some aspects that are based on good science. A National Research Council panel recently concluded that the last century brought a 0.6°C rise in surface temperature, but the prospect for the current century is for a rise of 3°C . One of the main suspected causes is accumulation of certain gases in the atmosphere. The magnitude of the effect is expressed as the global warming potential (GWP) of various gases. The EPA web site (epa.gov) explains that the GWP index translates the emissions of various gases into a common measure, in order to compare their likely effects. The basis is *relative radiative forcing*, which is a change in the balance between incoming solar radiation and outgoing infrared radiation. GWPs are calculated as the ratio of the radiative forcing that would result from the emissions of one kilogram of a greenhouse gas to that from

emission of one kilogram of CO_2 over a period of time (usually 100 years). The most recent GWPs (assigned in 1996) are: $\text{CO}_2 = 1$, $\text{CH}_4 = 21$, and $\text{N}_2\text{O} = 310$.

What do energy prices, severe limits on emissions, and global warming potential mean for landfill gas applications? The answer is complex but compelling. Landfills obviously generate CH_4 , which is a potential fuel, but also is potentially harmful to the environment. In a sense, CH_4 produced this way is renewable, since it is a byproduct of civilization. Hence, any CH_4 consumed from a landfill reduces the drain on the natural resource, and it is much better that it be burned in a useful way than merely allowed to escape into the atmosphere. Thus, it is important not to allow CH_4 to escape into the atmosphere, and it is foolish not to use it as fuel. Consequently, there are strong reasons to recover this CH_4 , based on environmental protection and energy efficiency. Presumably, if those are strong enough, there will also be an economic incentive, possibly on account of its inherent value or tax incentives.

As mentioned previously, both CH_4 and CO_2 are generated simultaneously. The mixture is not trivial to separate. Membranes, cryogenic distillation, and pressure swing adsorption (PSA) can be used, with the optimum determined by flow rate and composition. In addition, landfill gas is always saturated with water vapor, and it contains various impurities introduced mostly via permeation or leakage from discarded stuff.

There are two ends of the spectrum regarding CH₄ recovery. One is virtually passive, i.e., in which CH₄ that percolates upwards encounters a clay cap and most of it consequently flows into a manifold that lies just below the cap. A disadvantage of that approach is that a substantial amount CH₄ may reach the atmosphere via thin spots or cracks in the clay cap. The other end is similar, but employs vacuum to draw substantially all of the CH₄ into the manifold. In this case, a substantial amount of air penetrates the cap because the pressure is below that of the atmosphere. It turns out that the O₂ in air is consumed due to aerobic digestion near the surface. Nitrogen is not consumed but is delivered in the manifold along with CH₄ and CO₂, and various impurities. This creates an additional separation problem that was not addressed by Sircar and coworkers.

Potential Separation Schemes

The separation problems for landfill gas are associated with the significant components, of which there are five significant categories:

- CH₄ and other hydrocarbons that typically comprise about half of the stream,
- CO₂, which frequently comprises nearly remaining half of the stream and is more strongly adsorbed than CH₄,
- N₂ and O₂, which are generally less strongly adsorbed than CH₄ and which might comprise about 10% of the stream,
- H₂O, which is almost always at its saturation limit, and which potentially interferes with adsorption), and
- Noxious impurities such as VOCs, sulfur-, chlorine-, and silicon-bearing compounds, which might comprise 1% of the stream, but could pose operational problems even below 100 ppm.

Cryogenic distillation would be suitable for splitting the first three components, but would require a feed-dryer to prevent internal plugging due to frost. In all likelihood, the noxious impurities would be concentrated in the CO₂ product, which would probably make that product unusable, except for the crudest applications (e.g., oil recovery). A significant consideration for cryogenic distillation is that it does not adapt well to low flow rates (<20,000 Nm³/hr, i.e., about 10,000 to 12,000 scfm depending on whether based on

32°F, 60°F, or 70°F), such as would be expected at most landfills.

Membranes could be used to remove moisture and the bulk of the CO₂, and might remove some impurities, depending on the type of membrane. There are no known membranes, however, that exhibit much selectivity between N₂ and CH₄. Furthermore, membranes are not well suited for bulk separation such as CO₂ and CH₄, since only one relatively pure product is possible, and that only at moderate recovery. Consequently, it would not be practical to use a membrane to split CO₂ and CH₄. Besides, membranes do not scale-up well to high flow rates. That is, the cost per unit of gas processed tends to be rather flat.

Adsorption, on the other hand, can be used to split all the components. For example, it would probably be desirable to use thermal swing adsorption (TSA) to remove moisture, e.g., with silica gel or activated alumina. TSA could also be used to remove the impurities, e.g., with activated carbon. In that case, it would be prudent to remove moisture prior to the impurities, since activated carbon does not perform well at high humidity. Subsequently, PSA could be used to separate CO₂ as the more strongly adsorbed component from N₂ and CH₄, which are less strongly adsorbed, then the final stage could separate CH₄ from N₂. More will be said about this in the section on Process Design.

Quantitative Assessment

Choosing process technology is very complex, frequently involving experimental testing on various scales, economic analysis, possibly computer simulations, and so on. A complete discussion of all of those considerations is beyond the scope of this paper. Rather, the purpose here is to show, first, how major aspects affect the economics, and second, some simple relationships that may be employed to identify superior combinations of adsorbent and PSA operating conditions.

Economics

In the past, landfill applications have not been economically attractive, due to the amount of processing required and the low quantity of saleable gas. Some simple rules-of-thumb can be used to estimate overall economics, ignoring the removal of impurities such as H₂S and VOCs. They are based on historical data for processes built according to the second and third stages of either Fig. 3 or 4. As a specific example, consider:

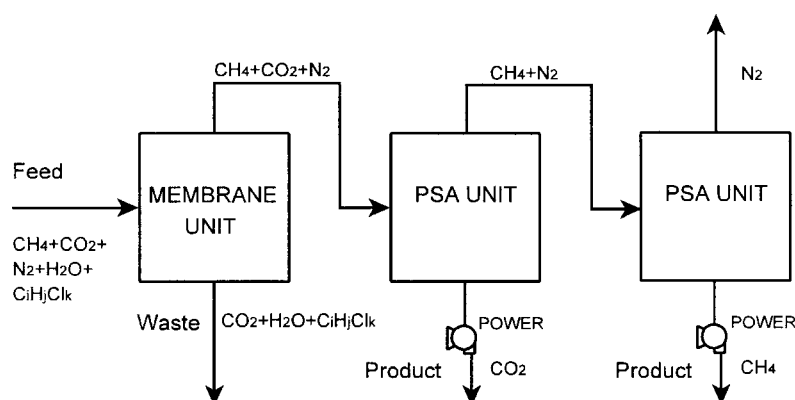


Figure 3. Schematic diagram of hybrid membrane/PSA system for splitting landfill gas.

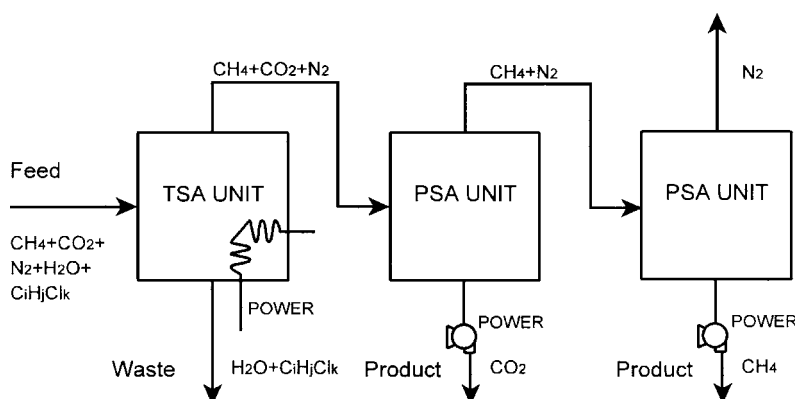


Figure 4. Schematic diagram of multistage adsorption process for splitting landfill gas.

50% CH₄, 33% N₂, 17% CO₂. Some approximate pro-rata costs are shown in Table 1 below.

Clearly, according to the values in the table, when the price of natural gas was about \$2.00 per 1,000 SCF, or (at a heating value of 1,000 Btu/SCF) \$2.00 per million

Btu, or \$1.90 per GJ, there was no way to split gas such as this and break-even.

In order for landfill gas to be viable economically, some of the following conditions must exist:

1. The price of pipeline quality "natural gas" must be higher than \$3.50/1000 SCF or \$3.50/million Btu,
2. There must be a nearby consumer of crude CO₂, and finally (3) Tax incentives must exist for (a) disposal of landfill gas, and/or (b) consumption of 'renewable' fuel rather than fossil fuel.

Table 1. Comparison of costs associated with LFG enrichment to pipeline quality.

Cost component	\$/10 ³ SCF	\$/10 ⁶ Btu	\$/10 ³ Nm ³	\$/10 ⁹ J
Collection & drying ^a	\$0.60	\$1.20	\$21.19	\$1.14
Feed compression ^b	\$0.15	\$0.30	\$5.30	\$0.28
CO ₂ rejection ^b	\$0.15	\$0.30	\$5.30	\$0.28
N ₂ rejection ^c	\$0.75	\$1.25	\$26.49	\$1.19
Product compression ^b	\$0.10	\$0.10	\$3.53	\$0.09
Transportation ^b	\$0.20	\$0.20	\$7.06	\$0.19
Total		\$3.35		\$3.18

^aUS EPA Doc. 430-B-96-0004, 1996.

^bProprietary field cost.

^cD'Amico et al. (1993).

Process Design

Two plausible potential flowsheets are shown in Figs. 3 and 4. The former would be promising for a single product, CH₄, and is functionally similar to Sircar's first process. It is a hybrid process: three stages consisting of a membrane stage to separate water vapor and organic impurities from the feed, followed by two PSA stages, i.e., a CO₂-rejection unit and a N₂-rejection unit.

All three stages consume power, though that for the membrane stage is small since water vapor, the organic impurities and even CO₂ are more permeable than are CH₄ and N₂. The main disadvantage for this approach is that the CO₂ product is not sufficiently pure to be salable.

Another three-stage flowsheet, shown in Fig. 4, would be promising to extract two products, CH₄ and CO₂, and is similar to Sircar's second process. It is a sequence of a TSA stage (to separate water vapor and organic impurities from the feed), followed by two PSA stages (a CO₂-rejection unit and a N₂-rejection unit). Though all three stages consume power, the frequency of the TSA system should be low, because the concentrations of water vapor and organic impurities are low, and the adsorption capacities are high. This process can produce CH₄, as well as CO₂, at high recovery. It also produces N₂ virtually free of CH₄, though that stream has no value.

In these flowsheets, CO₂ is removed first since it is generally more prominent and is more strongly adsorbed than CH₄. Consequently, it is more important to eliminate early, and is easier to remove than N₂, since it typically requires no power. Once CO₂ is removed, the remaining CH₄ mole fraction is 0.6024, assuming that essentially the same amounts of both components are lost by rejecting the CO₂. The final stage, the CH₄–N₂ split, does require power, and the cost of N₂ rejection is about 5 × that of CO₂ rejection, as shown in Table 1. Hence, it is the focus of the following discussion.

The two most important factors in designing a PSA system for a particular application, including the CH₄–N₂ split, are the required power and the adsorber volume, or equivalently, the mass of adsorbent. These dominate the operating expense and capital cost, respectively, are intimately related to other common scales of performance, and can be optimized with respect to various operating conditions and design choices. Secondary considerations include the type of adsorbent, the number and type of valves, maintenance, materials of construction, and so on. Though these are important, there is practically no way to present a systematic discussion of them. Consequently, this section will address the interplay between required power, adsorber volume and common scales of performance.

As a basis for quick, order-of-magnitude analysis, we will consider linear isotherms of a binary mixture, viz., $A = \text{CH}_4$ and $B = \text{N}_2$ (see Ch. 4 of Ruthven et al., 1994). That is, we will take the equilibrium

relationship to be:

$$q_i^* = k_i p_i \quad (1)$$

where q_i^* is the equilibrium capacity and p_i is the partial pressure of component i . Actual Henry's law slopes, k_i , for CH₄ and N₂ at 50°C are: 0.4204 mmol/g-bar and 0.1713 mmol/g-bar, respectively. Expressed in concentration terms, again for CH₄ and N₂ are 22.52 mol/m³_{solid}/mol/m³_{gas} and 9.18 mol/m³_{solid}/mol/m³_{gas}, respectively. Admittedly, the linear isotherm fits, especially for methane, are not very good, but they are probably adequate for process selection purposes.

The relevant scales of performance are:

- \mathcal{P}_i = Productivity of Component i = product flow rate $\times y_{ip}$ /amount of adsorbent;
- R_A = Recovery of A = average low pressure product flow rate $\times y_{ALP}$ /average feed flow rate $\times y_{AF}$;
- R_B = Recovery of B = average high pressure product flow rate $\times y_{BHP}$ /average feed flow rate $\times y_{BF}$.

For the cycle shown in Fig. 5, $y_{ALP} = 1$ and the intrinsic recoveries are:

$$R_A = 1 - (\wp(1 - \beta)y_{AF})^{-1} \quad (2)$$

$$R_B = 1 \quad (3)$$

where $\wp = P_H/P_L$, the ratio of absolute pressures, $\beta = \beta_A/\beta_B$, where the terms β_A and β_B can be determined via: $\beta_i = \varepsilon/[\varepsilon + (1 - \varepsilon)k_i]$, and where ε = overall void fraction = 0.747 for this particular activated carbon. Combining the isotherm slopes, we find $\beta_A = 0.1159$ and $\beta_B = 0.2434$, so $\beta = 0.4763$. One limit of performance is immediately evident: the minimum "break-even" pressure ratio at which $R_A = 0$, i.e., $\wp_{\min} = 1/(1 - \beta)y_{AF} = 3.17$. Above that pressure ratio, a net positive product is obtained, while below that value operation is infeasible.

Using the above definitions, the Productivity of CH₄, \mathcal{P}_A , is given by:

$$\mathcal{P} = K \frac{(1 - \beta)y_{AF} - 1/\wp}{n_{BEDS} V_{BED} \rho_B} \quad (4)$$

The power requirement for adiabatic compression of an ideal gas, Φ , is:

$$\Phi = \frac{\gamma}{\gamma - 1} \frac{QRT}{\eta} \left[\wp_C^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (5)$$

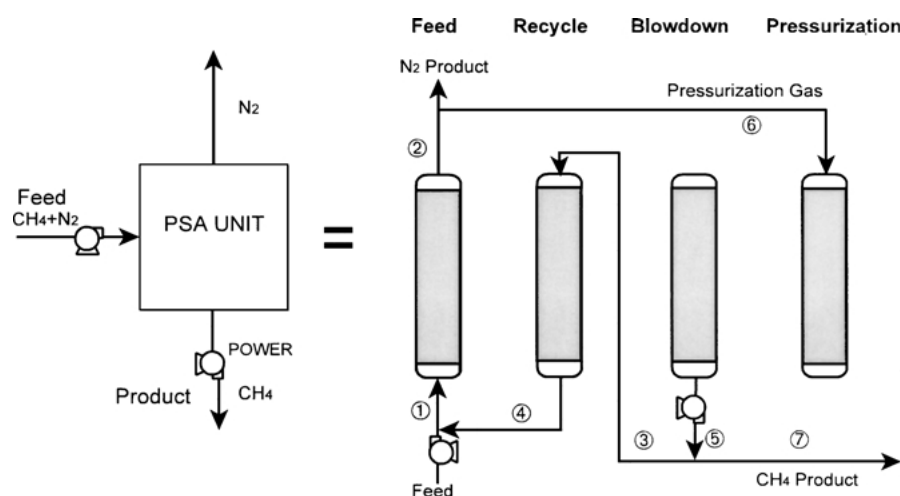


Figure 5. Schematic diagram of 3rd-stage: PSA process for splitting N_2 from CH_4 .

where γ is the ratio of specific heats at constant pressure and constant volume, Q is the molar flow rate, η is the mechanical efficiency, and ϕ_C is the compression ratio, P_{CH}/P_{CL} . For LFG with the 4-step cycle shown in Fig. 5, it would be expected to span above and below atmospheric pressure so that both a feed compressor and vacuum pump are needed, for example, with $P_H = P_{CH} \cong 5$ atm and $P_L = P_{CL} \cong 0.1$ atm. Neglecting efficiency differences between the vacuum pump and compressor, Φ may still be estimated from the above equation, with $\phi_C \cong \phi = P_H/P_L$.

Design decisions can be simplified by some rather simple observations. First, Φ and \mathcal{P}_A both increase as the pressure ratio, ϕ , increases. Hence, there will be an optimum pressure ratio to minimize total cost. Selection of the adsorbent is simplified by noticing that \mathcal{P}_A increases as the feed mole fraction, y_{AF} , increases, and as the selectivity, β , and amount of adsorbent, $n_{BEDS} V_{BED} \rho_B$, decrease. The amount of adsorbent will decrease as the Reynolds number increases, but that will result in higher pressure drop, and will also lead to a loss of selectivity. Hence, the amount of adsorbent cannot be reduced at will.

Summary

The previous work by Sircar and co-workers has stood the test of time: landfill gas (LFG) is growing in importance as a resource, particularly as a fuel. That work focused on two processes, one that removed carbon dioxide from methane, and another that produced two relatively pure streams. That is, the first one produced

CO_2 -free methane and the other produced both CO_2 -free methane and methane-free CO_2 . In both cases, the methane stream contained other light gases, such as nitrogen.

Two societal forces have boosted the incentives for exploiting it since the 1980s, the push to use renewable resources as fuel, and the *Kyoto Protocols*, which restrict production of greenhouse gases, e.g., encouraging conversion of methane in LFG to carbon dioxide. Consequently, new process technology has been developed to enable pipeline quality methane to be extracted from LFG. Two three-stage flowsheets are discussed as a means to accomplish the separation of pipeline-grade methane from LFG. One is a hybrid membrane—PSA system. The other is a TSA—PSA system. The third stage of both of these systems is crucial to obtaining pipeline quality gas, i.e., to extract the nitrogen and other light gases from methane. It consists of a novel PSA cycle that is explained in terms of: a model by which the recovery, power requirements, and adsorbent bed size can be estimated. Based on the equations presented, it is possible to estimate the economic return, based on the recovery, productivity, and power requirement.

Though there have been temporary periods of high natural gas prices in the recent past, the average price has remained too low to justify recovering methane from LFG without artificial incentives. Those artificial incentives could be in the form of taxes levied on natural gas derived from wells (non-renewable), or tax credits given to those who produce pipeline-grade methane from LFG.

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