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FUEL GAS PURIFICATION WITH PERMSELECTIVE MEMBRANES

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ABSTRACT

Production of fuel gas from biomass and recovery of flared gas from landfills, oil fields, coal mines, is hampered by the high cost of gas purification for the removal of CO_2 and H_2S. Membranes offer a potentially simple and attractive technique for on-site gas purification. Two membrane approaches have been considered for fuel gas purification - polymer films and facilitated transport - each with its own unique advantages. Polymer films can be made extremely thin (<500Å), and thus have high gas throughput and a very low membrane area requirement. Ultrathin polymer membranes have been found to be extremely attractive for purification of gas produced from waste or in remote site applications. Of particular interest is biogas produced from anaerobic digestion of sewage, municipal waste, agricultural waste, and landfills. Membrane purification is expected to cost less than half of that for conventional scrubbing processes. Additionally, the gas is purified and dried at the same time. Laboratory tests confirm that membrane performance projections can be met. Facilitated transport membranes in which reversible chemical reactions with a carrier species occur, have nearly perfect selectivity for CO_2 and other reactive gases. However, permeation rates are relatively low, and they are less attractive for flared gas/biogas purification.

FUEL GAS PURIFICATION WITH PERMSELECTIVE MEMBRANES

INTRODUCTION

In the future it can be expected that a substantial fraction of the gas used in the U.S. will originate from unconventional sources including substitute natural gas (SNG) from coal and biomass, and normally flared gas from anaerobic sewage treatment, landfills, oil fields, and coal mines, and agricultural waste digesters. A characteristic common to all these sources with the exception of the coal gasification and cultivated biomass SNG plants is that their output is low - 1,000 to 100,000 m^3/day. At this small scale gas purification - primarily CO_2, H_2S and H_2O removal - for subsequent fuel gas compression for storage or distribution is extremely costly with conventional technologies such as liquid absorption or solid adsorption. A membrane purification technique, which may substantially reduce the cost of purification, and thus make attractive the recovery of this gas, of this gas, is under development.

Membrane gas purification for SNG production from coal gas has also been studied. Membrane and gas scrubbing costs are estimated to be of the order of half that for liquid absorption systems (1).

Two different types of membranes have been under development for the separation of the acid gases H_2S and CO_2 from fuel gas stream-polymer membranes and immobilized liquid membranes.

This paper describes analytical and experimental studies of membrane acid gas scrubbing from fuel gas streams. The studies have been performed utilizing biomass digester gas as its basis, but can easily be extended to flared gas from oil fields or coal mines, since the problem is basically the same - the economic removal of CO_2, H_2S, and water vapor from a low pressure methane containing stream.

Biogas from anaerobic sewage and waste digesters and landfills is of the same general composition: 60% CH_4, 40% CO_2, some H_2S or ammonia, and water saturated. In order to put the gas into a local distribution pipeline or to compress the gas for on-site storage, it must be purified to approximately 98% CH_4, a few parts per million of H_2S and dried. Many commercial processes including molecular sieves, liquid absorbents, such as aqueous amine and potassium carbonate solutions, and non-aqueous organic absorbents, are available and, when coupled with drying processes, can easily meet purification standards. Although these processes are suitable for large scale gas processing (>3x10^6 nM^3/day), they are too expensive to be applied to the low gas production rate generally found in waste biomass digestion systems. A membrane process which promises to reduce purification costs by over 50% is being developed for this application.

ULTRATHIN MEMBRANES FOR METHANE PURIFICATION

Techniques have been developed for the preparation of ultrathin silicone/polycarbonate membranes (2) for use in oxygen nitrogen separation applications. Utilizing these techniques membrane composites with active membrane thicknesses as thin as 200Å can be fabricated and operated. Because of this capability, membranes with extremely high permeation rates, and thus, low membrane area requirements, can be fabricated.

General Electric polymeric film membrane designated MEM-079 has been shown to have excellent properties for the purification of fuel gas. These are listed in Table 1. Ultrathin MEM-079 membrane composites are being tested for this application.

TABLE 1

PERMEATION PROPERTIES OF MEM-079

Permeability, $\frac{cc}{cm^2 sec} \cdot \frac{cm\ thick}{cmHg\ P} \times 10^9$

N_2	CH_4	CO_2	H_2S	H_2O
0.35	0.44	8.4	4.5	100.0

In order to determine the capabilities and systems requirements for the purification of methane streams a number of systems configurations have been analyzed to determine membrane area requirements, pumping power, and the percentage of methane in the feed recovered in the product. Clearly an infinite number of variations in pressures, staging and recycle ratios can be devised. Five of these configurations are shown in Figure 1, and calculated membrane areas, power, and methane recovery are listed in Table 2. The study basis was:

Feed Composition - 38% CO_2, 62% CH_4
Product Composition - 2% CO_2, 98% CH_4
Feed Pressure - 5 atm. abs.

The simplest system is shown in Figure 1a. The feed gas is pressurized and passed over the membrane surface. A vacuum is applied to the low pressure side of the membrane to achieve high CO_2/CH_4 separation. This system has a low power requirement and requires very little membrane area. However, of the systems studied, the simple cycle achieves the lowest methane recovery. For processes where anaerobic biomass digesters are utilized, the lean gas stream can be utilized for process heat to warm the digester feedstock or, perhaps, as the pumping energy source. It should be noted that even for conventional processes such as the molecular sieve and hot potassium carbonate systems, applied to small scale biogas purification, methane energy recovery is relatively low due to low process selectivity or high energy requirements. Of particular interest from the membrane systems study is the result that very high methane recovery can be achieved through multistaging or recycling. This, of course, is achieved at the expense of increased membrane area or power consumption.

In order to determine the sensitivity of system performance to membrane selectivity and purification requirements an analytical examination of the single stage, simple cycle biogas gas purifier was performed for varying membrane selectivities. The results are shown in Figure 2, which shows the effect of CO_2/CH_4 separation factor on methane recovery for various product purities. In each

TABLE 2

MEMBRANE SYSTEMS REQUIREMENTS FOR PURIFICATION OF BIOGAS

Basis: 10,000 M^3/day Feed Gas
MEM-079 MEMBRANE

	FEED GAS	PRODUCT GAS
	38% CO_2 62% CH_4 Saturated	2% CO_2 98% CH_4 Dry

	MEMBRANE AREA, M^2	POWER, KW	%CH_4 RECOVERY
a. Simple Cycle	100	29.6	76
b. Single Stage with Pressurized Feed and Recycle	160	69.2	90
c. Single Stage with Low Pressure Feed and Recycle	790	22.9	80
d. Two Stage Simple Cycle	160	52.4	93
e. Two Stage Pressurized Feed and Recycle	130	56.7	98
f. Two Stage Low Pressure Feed with Recycle	890	40.8	97

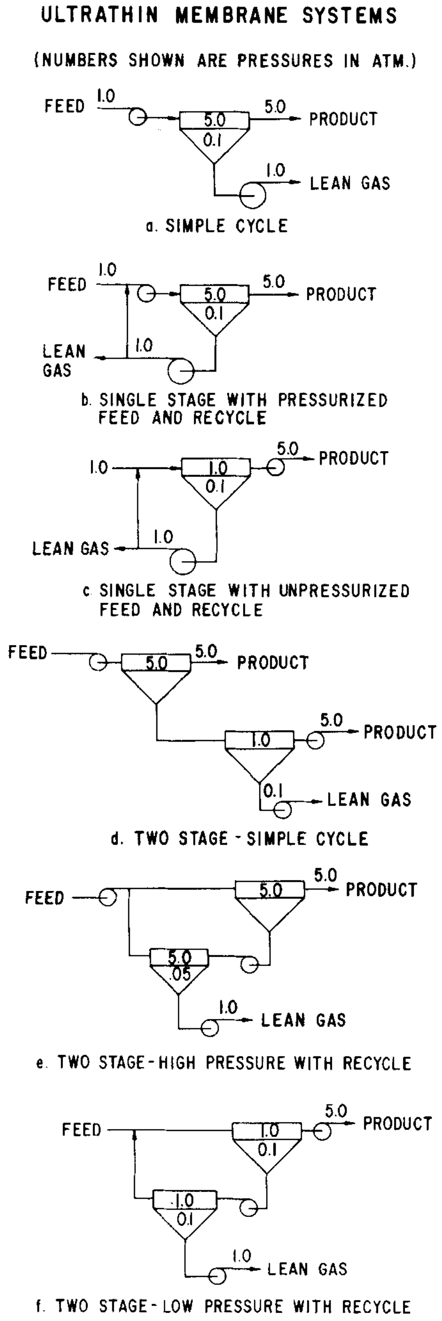

FIGURE 1 ULTRATHIN MEMBRANE SYSTEMS

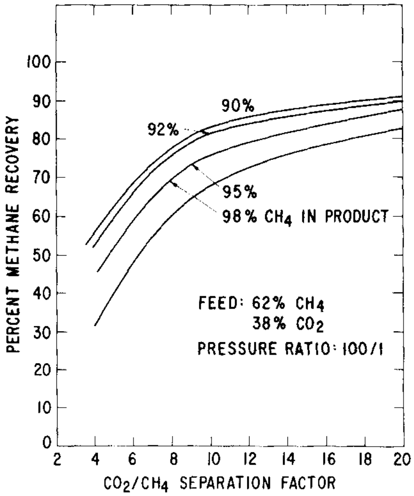

FIGURE 2 METHANE RECOVERY AS A FUNCTION OF CO_2 SELECTIVITY

case it was assumed that the transmembrane pressure ratio is 100:1. Several factors are apparent for this figure: (1) methane recovery is a strong function of the product purity requirements; (2) the effect of separation factor on methane recovery is relatively greater for values below about 10 than above about 10; (3) the effect of separation factor on methane recovery is much greater for high methane purity requirements.

Analytical results such as the above can be utilized to determine the relative importance of the various operating parameters which are available for the systems developer in order to produce the optimum system.

A cost analysis was performed based on the simple cycle membrane system. The technique utilized was consistent with the American Gas Association estimating method. The result of this cost analysis is shown in Figure 3, which includes information from a study performed by the Dynatech R/D Company for the Department of Energy (3). A data point for actual operation of a molecular sieve system on a landfill operated by Pacific Gas and Electric is

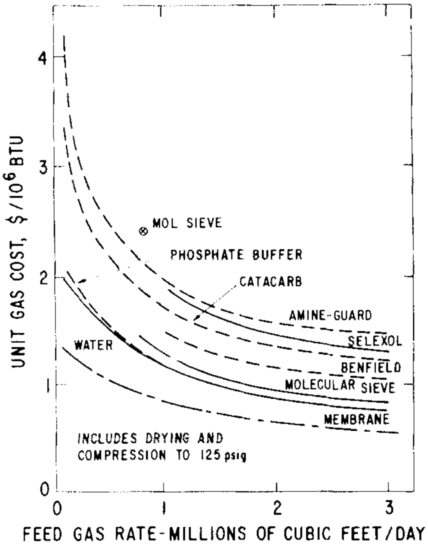

FIGURE 3 UNIT GAS COSTS FOR BIOGAS PURIFICATION

included (4). The membrane system shows clear cost advantages over the other processes, with water scrubbing being the next less expensive system.

Experimental Results

Laboratory tests have been performed to determine ultrathin polymeric film membrane permeation properties under expected operating conditions. These tests included vacuum permeation measurements on pure gases to determine the intrinsic separation properties of the membranes and flow tests at elevated pressures.

Vacuum permeation measurements were performed in the apparatus shown schematically in Figure 4. A 4-cm diameter membrane test specimen is clamped in a cell holder, in which the membrane composite is mechanically supported on a porous stainless steel frit. The test system is evacuated to a pressure level of approximately 1 micron, and the membrane allowed to out-gas. The test gas is then passed into the high pressure side of the membrane then isolated. The pressure rise due to gas permeation is monitored with a

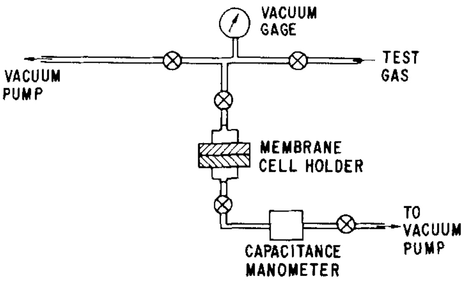

FIGURE 4 VACUUM MEMBRANE PERMEATION MEASUREMENT SYSTEM

Granville-Phillips capacitance manometer. The permeability, Pr is calculated using the equation:

$$Pr = \frac{N}{A} \times \frac{\delta}{\Delta P}$$

Where: N = Gas flow, std.cc/sec.
A = Membrane area, cm^2
δ = Membrane thickness, cm.
ΔP = Pressure difference, cm·Hg

Alternatively, when permeability values are known, the membrane thickness can be calculated. Membrane integrity can be determined by permeability ratios (separation factors) for various gases, which can be measured for thick films.

Results of these tests are shown on Table 3. The nitrogen permeability was used as the basis for the thickness calculations. Some deviation from the bulk polymer permeation properties was noted, for which two factors may contribute: (1) membrane damage may occur during assembly of the test cell, and (2) since the membranes are so thin, some effect of the ultrathin membrane support permeation resistance may have contributed to the overall composite permeation properties.

A series of laboratory tests was then performed utilizing a small, pressurized flow cell, to which gas mixtures were fed. A schematic diagram of the test system is shown in Figure 5. The pressurized feed mixtures are fed into the test cell, the pressure

TABLE 3

VACUUM PERMEATION RESULTS OF ULTRATHIN MEM 079 MEMBRANES

	Permeability, $\frac{cc}{cm^2 sec} \cdot \frac{cm\ thick}{cmHg\Delta P} \times 10^9$			Effective Thickness, Å
SAMPLE	N_2	CO_2	CH_4	
Bulk Polymer:	0.35	8.4	0.44	
1-25	0.35 (base)	7.08	0.51	1300
7-12	0.35	6.10	0.48	1600

SEPARATION FACTOR

	CO_2/N_2	CO_2/CH_4
Bulk Polymer:	24.0	19
1-25	20.2	13.9
7-12	17.4	12.7

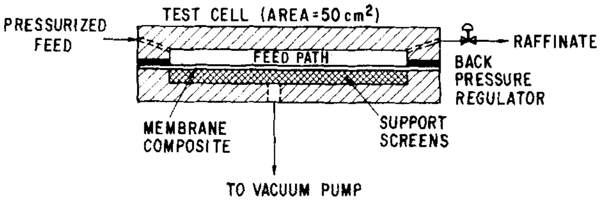

FIGURE 5 PRESSURIZED FLOW TEST SYSTEM

being controlled with a back pressure regulator and a vacuum applied to the low pressure side with a diaphragm vacuum pump. Typical conditions are 5 atm. abs. pressure on the feed and 0.2 atm. abs. on the extract side of the membrane. Nitrogen was sometimes used in place of CH_4 in the test gas for ease of operation. Results of some of these tests are shown in Table 4.

Considerable variation in the apparent separation factor for CO_2, CH_4 ($\alpha CO_2/CH_4$) was noticed. In general, measured $\alpha CO_2/CH_4$ values were somewhat lower than that measured on the bulk polymer using a thick membrane. Separation factors for the ultrathin composites ranged from 11.1 to 19.9 versus a bulk polymer value of 19, leading to slightly lower methane recoveries than predicted from the systems study. For $\alpha CO_2/CH_4 = 11$ the methane recovery will be 65% at 98% product purity, for $\alpha CO_2/CH_4 = 14.7$ it will be 73%, and for $\alpha CO_2/CH_4 = 17.2$ the methane recovery will be 75% versus 76% for a separation factor of 19. It is felt that to be attractive, the separation factor, $\alpha CO_2/CH_4$, must be greater than 10.

It can be concluded from these tests that the assumed membrane performance values utilized in the system study can at least be approached by membranes operating under realistic pressures and CO_2 removal requirements.

In order to evaluate the scale-up of the membrane system, a multi-layer $0.56 m^2$ (6 sq. ft.) membrane stack composed of $6-0.09 m^2$ (1 sq. ft.) unit cells was assembled. The cells were arranged such that the feed channel was continuous to ensure good flow distribution over the membrane surfaces. Operating results for the membrane system are shown on Table 5. For most of the testing CO_2/N_2 mixtures were utilized because of difficulty of handling large quantities of methane in the laboratory. Results were very similar to those of 50 cm^2 flow cell tests. Thus, the degree of confidence in our ability to achieve performance goals with scaled-up membrane systems is much enhanced.

A 6-layer membrane module is presently undergoing field testing on sewage digester gas. Results will be reported in a future paper.

TABLE 4

ULTRATHIN MEM 079 MEMBRANE FLOW TESTS

AREA = 50 cm^2

	FEED COMPOSITION,%			PRESSURES,atm		% CO_2		APPARENT SEPARATION FACTOR		EFFECTIVE MEMBRANE
TEST	CO_2	CH_4	N_2	FEED	EXTRACT	RAFFINATE	EXTRACT	CO_2/CH_4	CO_2/N_2	THICKNESS, Å
1-25	40	-	60	5	0.3	3.0	77	-	17.5	1300
3-16	38	62	-	5	0.2	2.1	66	11.1	-	-
	40	-	60	5	0.2	2.3	74	-	18.6	-
3-27	38	62	-	5	0.2	1.0	65	12.3	-	-
3-28	38	62	-	5	0.1	3.9	73.4	19.9	-	930
	38	62	-	7.8	0.1	3.7	66.9	11.8	-	-
4-4	38	62	-	5	0.2	7.9	76.0	12.8	-	1310
4-13	38	62	-	5	0.1	0.9	58.7	14.7	-	880
5-2	38	62	-	5	0.1	1.3	69.5	17.2	-	1090

TABLE 5

LABORATORY TEST OF 0.56M^2 MULTILAYER MEM-079 MEMBRANE STACK

FEED COMPOSITION,%			PRESSURES, atm		FLOWS,cc/sec			% CO_2		APPARENT SEPARATION FACTOR	
CO_2	CH_4	N_2	FEED	EXTRACT	FEED	RAFFINATE	EXTRACT	RAFFINATE	EXTRACT	CO_2/N_2	CO_2/CH_4
60	-	40	4.8	0.2	500	244	256	5.2	74.9	26.5	-
60	-	40	4.8	0.2	370	155	219	2.8	68.5	21.0	-
60	-	40	4.8	0.2	513	264	249	6.3	76.3	21.4	-
62	38	-	4.8	0.3	468	264	204	6.1	67.3	-	13.6

IMMOBILIZED LIQUID FACILITATED TRANSPORT MEMBRANES FOR FUEL GAS PURIFICATION

The facilitated transport of CO_2 and H_2S through aqueous carbonate immobilized liquid membranes has been discussed in a number of publications (5,6,7). Extremely high selectivities for gases which undergo facilitated transport over non-reacting gases are achieved; thus, these membranes can scrub acid gases from fuel gas streams while achieving nearly complete recovery of methane.

The membranes consist of a hydrophilic porous polymer matrix membrane whose pores are filled with an aqueous carbonate solution. Matrix membranes which can withstand in excess of 20 atm. transmembrane pressure differentials before the liquid is expelled have been developed. The immobilized liquid membrane is then supported on a hydrophobic porous support membrane which further assists in the prevention of liquid expulsion.

A fuel gas purification system incorporating the immobilized liquid facilitated transport membrane is shown schematically in Figure 6. The feed gas, which is normally saturated, is conditioned so that it's water vapor pressure is in balance with the vapor pressure of the membrane liquid and is passed over one side of the membrane. The permeating CO_2 is then flushed out of the extract side of the membrane package with a sweep gas, which has been humidified to the appropriate water vapor partial pressure. Humidity control is necessary to prevent drying or dilution by condensation of the membrane liquid.

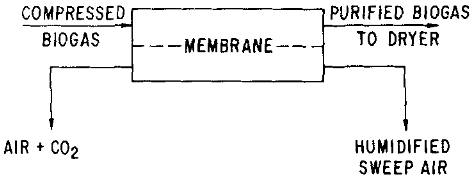

FIGURE 6 SCHEMATIC DIAGRAM OF AN IMMOBILIZED MEMBRANE BIOGAS PURIFIER

In order to assess the applicability of facilitated membranes to fuel gas purification, CO_2 permeabilities were measured over a range of operating conditions expected in biogas systems. Of particular interest were membrane permeability, which defines the area requirement, and the tolerance of the ILM to humidity variations.

Unlike simple solution/diffusion membranes, facilitated transport membranes exhibit a complex relationship to operating conditions because of the chemical reactions which occur. Permeability is a function of the following parameters:

- temperature
- acid gas partial pressure
- acid gas transmembrane partial pressure difference
- relative humidity
- catalyst
- membrane thickness

The test membranes consisted of K_2CO_3 and Cs_2CO_3 solutions immobilized in a porous cellulose matrix membrane, which was then supported on Goretex® porous fluorocarbon or Celgard® porous polypropylene membranes. CO_2 hydrolysis catalysts were also utilized, since they have been shown to substantially increase CO_2 permeabilities in an earlier study (8). This composite was mechanically supported on fine mesh screens. A sketch of the test cell is shown in Figure 7. The test cell was then incorporated into the test system shown schematically in Figure 8. Mixtures of CO_2 and CH_4, occasionally with some H_2S, were passed through a humidifier, which consisted of a sparger in a small pressure vessel submerged in a bath carefully maintained at the desired temperature. The bath temperature controlled the humidity of the gas stream. The sweep gas, generally He for ease of analysis, was similarly humidified and passed counter-

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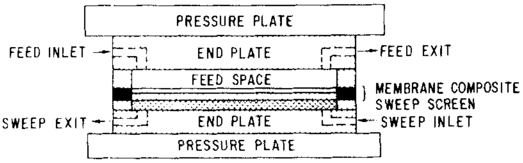

FIGURE 7 IMMOBILIZED LIQUID MEMBRANE TEST CELL

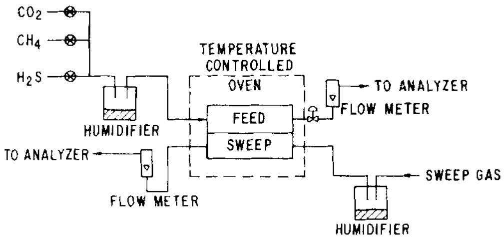

FIGURE 8 SCHEMATIC DIAGRAM OF THE IMMOBILIZED LIQUID MEMBRANE TEST SYSTEM

currently through the sweep side. The gas flowrates were measured and the compositions analyzed with a gas chromatograph.

Permeability results are summarized in Figure 9. As expected, and as reported in an earlier study (9), a substantial effect of CO_2 partial pressure on permeability was noted. This is due to the "saturation effect" resulting in increased apparent diffusional resistance at higher CO_2 partial pressures. Doubling the Cs_2CO_3 concentration from 35 to 70 in order to increase the CO_2 carrier capacity, however resulted in decreased, rather than increased permeabilities due to precipitation of the less soluble HCO_3^-. A substantially increased permeability was achieved by increasing the operating temperature from 40 to 50° due to an increase in CO_2 absorption rate.

No significant differences between Cs_2CO_3 and K_2CO_3 solutions of the same molar concentrations was noticed, nor did the $TeO_3^=$ catalyst give substantial differences in CO_2 permeability compared to the Catacarb® catalyst.

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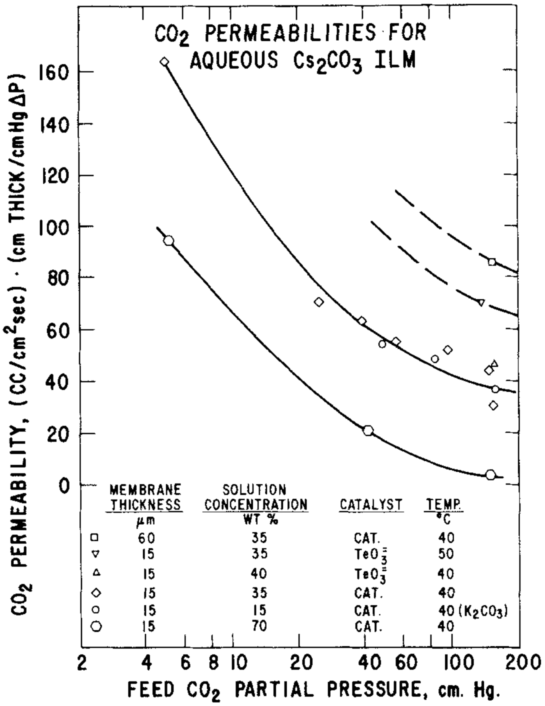

FIGURE 9 CO_2 PERMEABILITIES FOR AQUEOUS Cs_2CO_3 ILM

In order to determine the relative amounts of reaction and diffusion control of the permeation rate, the membrane thickness was increased by a factor of 4. Due to the way the permeability is defined, in a membrane where permeation is totally diffusion controlled there will be no effect of thickness on permeability; in a totally reaction rate controlled membrane the permeability will vary as the thickness. In Figure 9, it can be seen that the permeability approximately doubled for an increase in thickness by a factor of 4. It can be inferred then that both diffusion and reaction rates are important and that permeation rate increases can be achieved if thinner facilitated transport could be manufactured and operated under biogas conditions.

The effect of the relative humidities of the feed and sweep gases were assessed, and found to be substantially greater than that experienced in tests at higher temperatures (90-130°C) and pressures (22 atm total pressure). A relative humidity of 90% was found to optimum. The criticality of humidity control, particularly since large fractions of the feed gas flow are removed, makes operation of a practical system more difficult and represents a serious drawback of the ILM system.

Utilizing the above data, the membrane area requirement for a hypothetical purification system was determined. For a feed rate of 2800 nM^3/day, a rate typical of a small sewage digester, the membrane compared to the polymer film. Since the membrane is nearly perfectly selective for acid gases, methane recovery is in excess of 99%.

If techniques were available for the fabrication of thinner immobilized liquid membranes and reaction rates could be increased through the incorporation of a better CO_2 hydrolysis catalyst or higher temperature operation the high selectivity of these membranes would make them extremely attractive for fuel gas purification. Indeed, an earlier study has shown a substantial advantage of ILM CO_2 scrubbing over conventional processes (9).

CONCLUSION

Ultrathin polymer membranes have been shown to be an extremely promising method for the purification of biomass digester gas and flared gas in analytical and experimental studies. Successful development of the membrane system will result in a gas purification process in which scrubbing costs are less than half that for conventional processes. Field tests have been initiated in order to determine potential operating problems which may be encountered due to trace gas components.

Immobilized liquid facilitated transport membranes are less attractive for these types of applications, although they show promise for coal based SNG production. Permeation rates are limited by low CO_2 absorption rates at near ambient temperatures, and by thickness limitations.

ACKNOWLEDGEMENT

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