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Membrane selective exchange process for dilute methane recovery

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ABSTRACT

Methane gas is a valuable energy resource. Methane emissions are the second largest human-caused contributor to global warming. Significant quantities of the methane emissions are vented as carbon dioxide/methane mixtures from landfills and natural gas processing plants, since they are too dilute to burn or flare. This paper describes a novel membrane selective exchange process to upgrade dilute methane emission streams into useful fuel by removing CO_2 and introducing oxygen into the methane product stream. This is achieved in a single step without the need for compression. Flat sheet thin film composite membranes based on perfluoropolymers and a spiral-wound module were prepared and tested with model dilute methane mixtures. A technical and economic analysis shows that the selective exchange process is cost-effective, improves methane utilization and reduces global warming emissions.

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1. Introduction

Methane emissions are the second largest contributor to global warming, after carbon dioxide (CO_2), accounting for 10% of U.S. greenhouse gas emissions [1,2]. Due to increasing public awareness during the past two decades, various technologies and process improvements have been developed to curb methane emissions. However, dilute methane emissions containing 5–40 vol% methane are problematic because they do not burn [3]. Such streams often contain CO_2; for example,

1. older, closed landfill sites have methane emission streams with methane contents as low as 20%, with the remainder of the stream being comprised of CO_2 and nitrogen [4];
2. carbon dioxide removal units (amine absorption or membrane systems) in natural gas processing systems have vent streams containing 5-20% methane, with the balance composed of CO_2 [5,6].

Streams containing less than 40% methane have an energy content of less than 400 Btu/scf, which is too low for the streams to be burned or flared economically [7]. As a result, they are often vented, increasing global warming. The current unrecovered methane emissions from these sources are estimated at 1.0 million metric tons or 50 billion scf (standard cubic feet) per year in the U. S. alone [4,8]. With 7.6 times the global warming effect of an equivalent volume of CO_2, these methane emissions are equivalent to emissions of 21 Tg CO_2 per year. For comparison, a 600 MW_e coal-fired power plant emits about 4.0 Tg CO_2 per year [9]. Therefore, if the methane emissions from the above sources can be recovered and used, it would be equivalent to capturing and sequestering CO_2 from five 600 MW_e coal-fired power plants.

Table 1 compares treatment options and their global warming potential (GWP) for a typical dilute methane stream containing 20% methane. GWP is a measure of the heat that a gas traps over a certain period of time (usually 100 years), compared to CO_2 [2]. The larger the GWP value, the more warming the gas causes. CO_2 and methane have GWP values of 1 and 7.6, respectively. If the stream is simply vented without treatment, the methane content is responsible for 66% of the GWP of the whole stream, even though the methane content is only 20%. The dilute methane streams can be mixed with supplemental fuel to bring them to 500 Btu/scf so they can be flared, which reduces the GWP by 31% (see Table 1). However, this approach requires additional methane, adding significantly to the cost. The best solution would be to burn the stream as fuel, without adding any additional methane. If this is possible, the GWP could be reduced by 66% and the cost of separation could be compensated for or even covered by the value of the fuel produced.

Conventional CO_2 separation technologies (such as amine absorption, pressure swing adsorption and membrane technology) cannot recover methane economically from these dilute streams [10]. The CO_2 content (60–90%) of the gas is too high for economic

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Table 1
Options for dealing with 1 volume of dilute methane emission containing 20% methane and 80% CO_2, and the resulting global warming potential (GWP).

Options	Emission composition	Volume	GWP of emission	GWP reduction
Vent	20% CH_4/80% CO_2	1	2.32[a]	–
Flare requiring additional 0.6 volume of CH_4	100% CO_2	1.6	1.6	31%
Upgrade to fuel without additional CH_4	100% CO_2	0.8[b]	0.8[b]	66%

[a] GWP for untreated emission vent is calculated as $1 \times 0.2 \times 7.6 + 1 \times 0.8 \times 1.0 = 2.32$.

[b] Credit is taken for the 0.2 volume of methane usefully combusted.

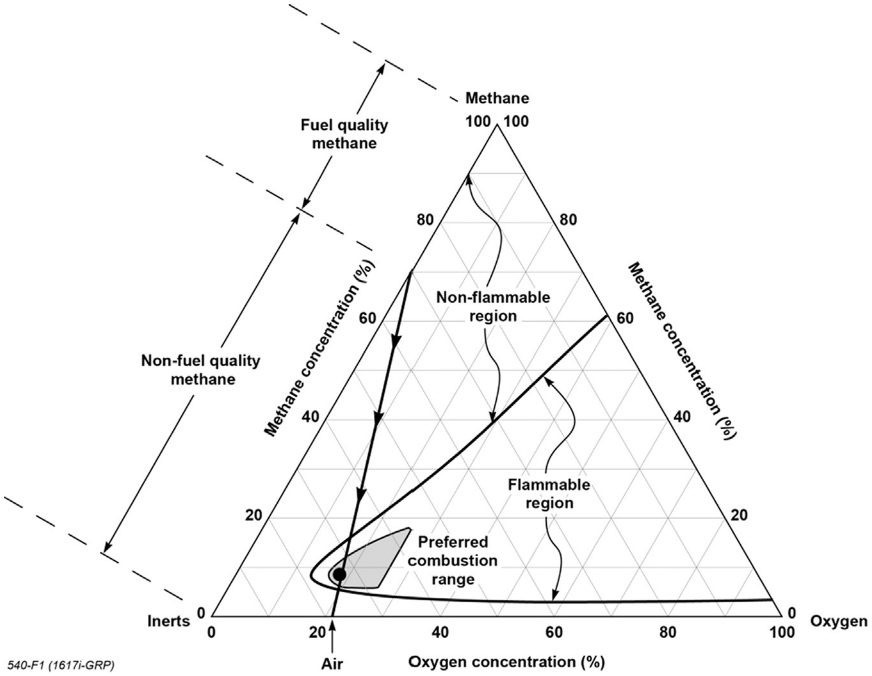

Fig. 1. Ternary composition diagram showing the flammable region and the preferred combustion range for methane/oxygen/inert gas mixtures [12,13]. Methane/inert gas mixtures with more than 70% methane can be used directly as fuel. Dilute methane streams with less than 70% methane cannot be easily burned with ordinary air and need methane upgrading to be used as fuel [7].

use of amine absorption or pressure swing adsorption, because the cost of the sorption system is usually proportional to the amount of CO_2 to be removed [6,10]. The low feed pressures (less than 50 psig) mean that conventional membrane systems are not an attractive option either, because large membrane areas will be required [11].

In this paper, we describe a novel membrane selective exchange process to upgrade the quality of the dilute methane/CO_2 streams. Using air as a sweep on the permeate side, the membrane removes CO_2 from the dilute methane stream, while introducing oxygen to the upgraded methane stream. The upgraded methane gas is thus combustible when mixed with ordinary air, and can be used as fuel for an engine, heater or boiler. The process reduces global warming emissions, and converts what was previously a waste stream into useful fuel in a potentially economical manner.

2. Background

2.1. Combustion of methane/inert mixtures

Combustion of methane-containing gas mixtures can be described using a ternary diagram of the type shown in Fig. 1 [3,12,13]. In this figure, the three components are methane, oxygen, and an inert gas, where the inert gas in this case is the summed concentrations of nitrogen and CO_2. The apexes of the triangle represent pure methane, pure oxygen and pure inert gas. Binary mixtures are represented by positions along the sides of the triangle. Mixtures of all three components are represented by points within the triangle; each mixture is represented by a single point.

The diagram is divided into two regions – the flammable region, where combustion is possible, and the non-flammable region, where it is not. The flammable region has a low content of inerts, and balanced concentrations of oxygen and methane. A small preferred combustion region within the flammable region is also shown. The preferred region is away from the edges of the flammable region, to ensure that minor concentration fluctuations do not take the mixture outside the flammable region and stall combustion. The preferred region is also relatively lean in oxygen (below 28%) to avoid excessive combustion temperatures, which lead to NO_x formation and create materials-of-construction issues [14,15].

In a ternary diagram, all gas compositions that can be obtained by combining two gas mixtures of different compositions are represented by a straight line connecting the two gas mixture compositions. Following this rule, as shown in Fig. 1, any binary methane/inert gas mixture containing more than 70% methane can be mixed with ordinary air to form a mixture that is within the preferred combustion range. The lines connecting binary mixtures containing less than 70% methane-in-inerts and air do not pass comfortably through the preferred combustion region. Therefore, these mixtures cannot be easily burned in air. Moreover, the presence of high content inerts often decreases the

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