

Natural gas sweetening polymeric membrane: Established optimum operating condition at 70% of CO₂ concentration feed gas stream

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Abstract

PETRONAS embarks on a breakthrough technology for natural gas sweetening in high CO₂ gas fields. Membrane technology is found to be a promising technology for bulk CO₂ removal from natural gas. It can be suited to wide operating conditions to process varied natural gas composition, pressure, and temperature. This paper focuses on the extensive development of PETRONAS in-house membrane and its evaluation for gas separation performance for high CO₂ feed gas at different operating conditions; e.g. feed gas flowrate, temperature, pressure, CO₂ concentration in mixed gas system, and permeate pressure. For all the cases in this study, samples were tested at optimum gas flowrate of 1000 standard cm³/min (sccm) to obtain representative membrane performance. Feed gas pressure and CO₂ concentration have shown significant effect on membrane permeation properties, whereas feed gas temperature and permeate pressure showed negligible impact. There is a trade-off between permeance and selectivity when CO₂ concentration is increased from 40% to 70%, where the CO₂ permeance increased by 12% which consequently reduces CO₂/CH₄ selectivity by 15%. In summary, the membrane developed in this study demonstrates high pressure durability up to 50 bar and temperature up to 55 °C with satisfactory gas separation performance in the presence of high CO₂ concentration in feed gas (up to 70% CO₂). This work is a breakthrough in establishing the operational boundary of PETRONAS Membrane for technology development and deployment in monetizing high CO₂ gas field.

Keywords: Natural gas, CO₂ removal, binary gas, mixed gas

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INTRODUCTION

Processing of natural gas is considered as the largest industrial gas separation application leading to the total worldwide natural gas consumption at about 95 trillion SCF/year [1]. Thus, to secure the worldwide natural gas demand, development of high CO₂ field is required. However, it is not economical to develop high CO₂ offshore fields due to high Capital Expenditure (CAPEX) of conventional proprietary Acid Gas Removal (AGR) system; Amine Absorption System which normally use for low CO₂ content gas removal application. In order to economically develop these high CO₂ gas fields, cost-effective CO₂ removal technology needs to be developed especially for offshore application. One of the technologies for CO₂ removal which is of particular interest is via membrane. Membrane advantages over other conventional technology which rely upon the operating cost, ease of operation [2], environmental consideration, space, and weight saving [3] for offshore and onshore installations.

Among all membrane configurations, hollow fiber membrane is preferred for offshore installations due to its unique characteristic with high packing density and high surface area to volume [4] which is critical in determining the CO₂ separation footprint for offshore installation. Furthermore, it has been reported that generally hollow fiber membrane modules were estimated to have an order of magnitude reduction in system footprint relative to spiral wound modules which make them an attractive in space-constrained

condition [5]. However, the fabrication of hollow fiber membrane with mechanically robust porous supporting layer, desirable separation, and defect-free selective layer without additional coating is challenging [6] [7]. This was due to extensive parameters involved in the membrane preparation process which include dope formulation, spinning condition, and post-treatment of spun fibers. Moving towards scaling up the hollow fiber production, extensive laboratory testing needs to be conducted. Thus, this paper presents the summary of the fiber performance testing results conducted by research team. These results would be critical in determining the preliminary operational boundary for the developed fiber.

EXPERIMENTAL

The schematic diagram of hollow fiber gas separation testing apparatus as shown in Fig. 1 was fabricated in order to evaluate the performance of hollow fiber at various operating conditions. This setup was used to evaluate the effect of different CO₂ concentration level, binary and mixed gas composition, feed flow rate, operating feed pressure, and operating permeate pressure. The performance of a membrane is mainly characterized by selectivity and permeance. The permeance (P/l) is simply the pressure normalized flux that measured asymmetric membrane productivity. The prepared hollow fibers were arranged in bundles and potted into Swagelok stainless steel tubing. Prior conducting the performance evaluation, quality control was

conducted to determine the hollow fiber ideal selectivity. The ideal selectivity is defined as ratio of permeance of two pure gases. The permeance of pure gases are pre-determined at feed pressure of 7 barg using Equation 1 and Equation 2. The total gas permeation rate was measured in the permeate side at atmospheric pressure and room temperature. The tested samples were verified to have at least 80% of Polysulfone's selectivity (CO₂/CH₄) intrinsic value that is 28.1 [8] prior actual performance evaluation.

$$\left(\frac{P}{l}\right)_x = \frac{Q_x}{\Delta P_x \cdot A} \tag{Equation 1}$$

$$\alpha_{(x/y)} = \frac{(P/l)_x}{(P/l)_y} \tag{Equation 2}$$

Where;

- (P/l)_x = Permeance of component (cm³/s.cmHg.cm²)
- Q_x = Permeate flowrate of component (cm³/s)
- P_x = Differential pressure of component (cmHg)
- A = Membrane active area (cm²)
- X_y = Component

$$\Delta P_{FRx} = \frac{P_F X_{Fx} - P_R X_{Rx}}{\ln\left(\frac{P_F X_{Fx}}{P_R X_{Rx}}\right)} \tag{Equation 4}$$

$$P_{Px} = P_p X_{Px} \tag{Equation 5}$$

where

- P_x = Differential pressure of component x (barg)
- P_{FRx} = Mean differential different of component between feed and residue (barg)
- P_F = Feed pressure (barg)
- X_{Fx} = Component concentration in feed stream (mol%)
- P_R = Residue pressure (barg)
- X_{Rx} = Component concentration in residue stream (mol%)
- P_{Px} = Permeate component pressure (barg)
- P_p = Permeate pressure (barg)
- X_{Px} = Component concentration in permeate stream (mol%)

RESULTS AND DISCUSSION

Effect of Feed Flow Rate

Fig. 2 depicts the effect of feed flowrate towards membrane permeation properties. An optimum flow rate between 700 sccm to 1000 sccm is required to evaluate the membrane performance. Further reducing the feed flowrate towards 200 sccm has resulted in about 23% declination in membrane performance while increasing of membrane stage cut up to 40%. This observations could be explained via increasing of mass transfer resistance across the fiber due to accumulation of larger molecules components at membrane surface area known as concentration polarization phenomena. Thus, the smallest molecule like CO₂ will have negative impact to its permeation rate resulted in reduced components permeance and membrane selectivity. Further determining the Reynolds number in the membrane housing indicated significantly lowered figured that is below 50 for feed flowrate of 200 sccm. Table 1 highlights the Reynolds number in membrane housing at different feed flowrates.

Table 1: Reynolds number in membrane housing for different feed flowrates

Feed flowrate (SCCM)	Reynolds Number
200	48.80
700	170.80
1000	243.99
2000	487.99
3000	731.98
4000	975.97

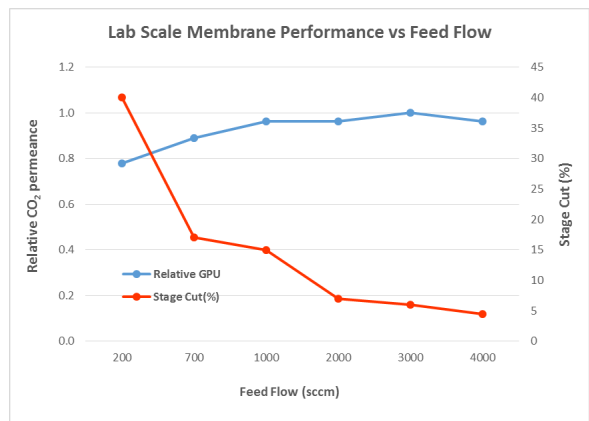


Fig. 2: Membrane performance at different feed flowrates.

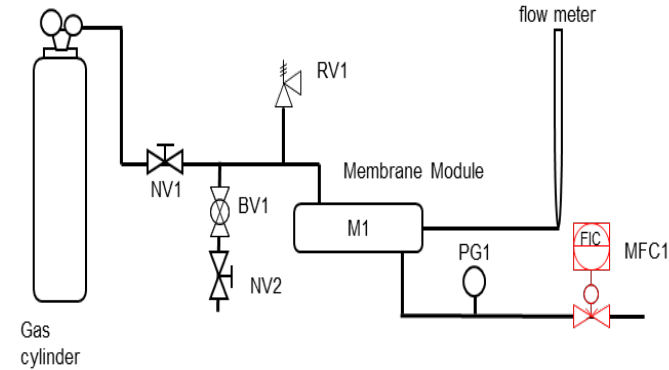


Fig. 1: Hollow fiber membrane test unit setup

The binary and mixed gases used were certified mixture of: 1) 40% CO₂ & 60% CH₄; 2) 70% CO₂ & 30% CH₄; 3) 40% CO₂, 0.5% N₂, 53.2% C1, 2.0% C2, & 1.6% C3; 4) 70% CO₂, 0.2% N₂, 28.6% C1, 1.0% C2, & 0.4% C3. The prepared hollow fiber samples were then subjected to mixed gas testing with feed pressure ranging from 20 barg to 60 barg. Further variation of feed flow rate ranging from 200 standard cubic centimeters per minute (sccm) to 4000 sccm is performed to understand flow hydraulic impact to fiber permeance and selectivity properties. In addition, the permeate pressure are varied from 0 barg to 4 barg by manipulating its back pressure. The feed gas temperature is varied between 25 °C to 55 °C to understand the fiber permeation properties. While, the CO₂ concentration are varied from 15% to 70%.

In order to determine the hollow fiber permeance and selectivity for a mixed gas system, it is necessary to quantify the gas composition in feed, non-permeate, and permeate stream. The quantification process was accomplished by using gas chromatography (Micro GC model Agilent 490). Equation 1 is then further expanded to Equations 3, 4, and 5 to calculate the gas components permeance for mixed gases system. While, the hollow fiber selectivity was determined as per Equation 2.

$$\Delta P_x = \Delta P_{FRx} - P_{Px} \tag{Equation 3}$$

Effect of CO₂ concentration in feed stream The membrane are exposed to CO₂ concentration ranging from 15% to 70% at different feed pressure from 20 barg to 50 barg. It is well known in literature that CO₂ would act as a plasticizer for polymeric membrane. Theoretically, the higher CO₂ concentration in membrane would increase the polymer free volume and segmental mobility that would result in the declining of membrane selectivity.

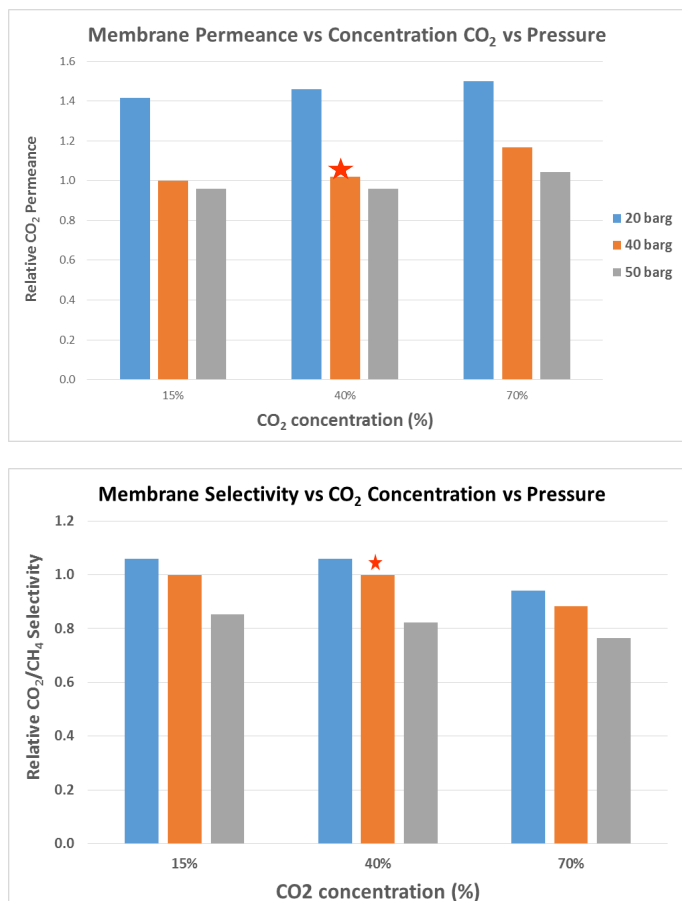


Fig. 3: Membrane performance at different CO₂ concentration and feed pressure (★ = base value).

As highlighted in Fig. 3, generally CO₂ permeance is gradually increased as the CO₂ concentration increased and vice versa for the membrane selectivity. In addition, for CO₂ concentration below 40%, the CO₂ permeance increment is insignificant (about 5%) as compared to CO₂ concentration above 40% (about 12%) at similar operating conditions. However, the trend of membrane selectivity showed significant reduction going from 40% CO₂ to 70% CO₂ (about 15%).

Previous work has tabulated polysulfone (Psf) as one of the materials that has high CO₂ plasticization pressure as compared to other commercial polymers [13]. Therefore, this polymer has a potential to be used for high CO₂ environment based on the results depicted in Fig. 3 for 70% CO₂ case.

Effect of feed gas temperature

This study are focusing to membrane with feed temperature ranging from 25 °C to 55 °C that would cover typical range of membrane operation. As depicted in Fig. 4, its CO₂ permeance is gradually increased as the feed temperature is increased from 25 °C to 55 °C. Nevertheless, the membrane selectivity is gradually reduced with increased of feed gas temperature. However, the membrane separation performance reduction is less than 5%. This observation could be explained via either (i) increment of segmental mobility of polymer network and/or (ii) higher activation energy of components. Both effects could result in increments of components diffusion across

the membrane. Although permeation of CO₂ and CH₄ are relatively increased with increased of temperature, the higher increment rate of CH₄ as compared to CO₂ has resulted in reduction of membrane selectivity.

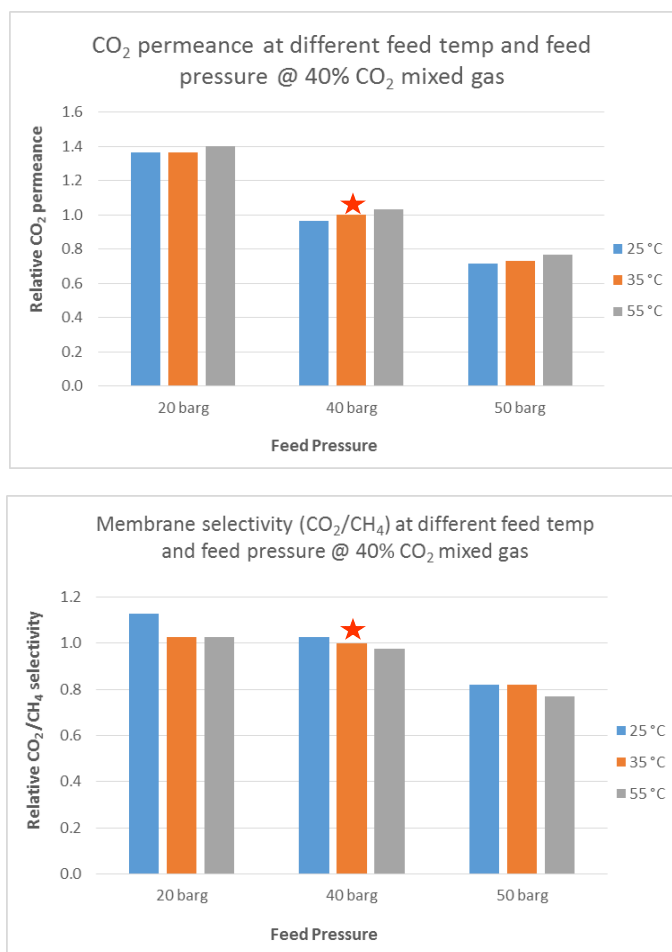


Fig. 4: Membrane performance at different feed temperature and pressure (★ = base value)

Effect of feed pressure

The membrane durability was evaluated using feed pressure ranging from 20 barg to 60 barg to evaluate its maximum operating pressure envelope. As depicted in Figure 5, the membrane performance indicator for both permeance and selectivity have been significantly affected as the feed pressure increased towards 60 barg. Referring to Fig. 5, the membrane performance is reduced more than 30% as the feed pressure increased from 20 barg to 40 barg. Furthermore, based

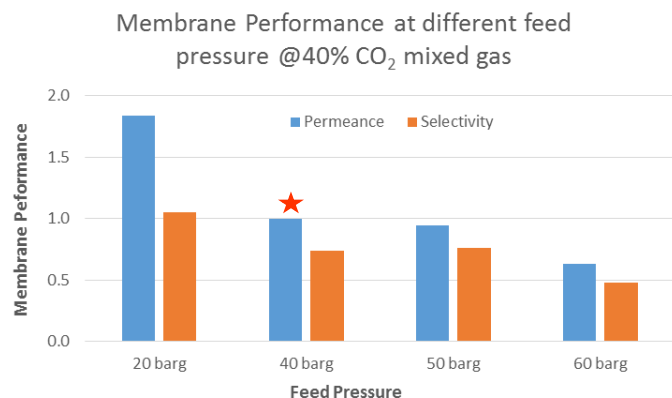


Fig. 5: Membrane performance at different feed pressure (★ = base value)

on the result, it is clearly indicated the membrane could not efficiently performed CO₂ separation at 60 barg as both permeance and selectivity reduced more than 60% as compared to the performance at 20 barg.

This observation could be explained via the potential deterioration of fibers as resulted in reduction of fiber's mechanical properties at elevated pressure. Hypothetically, the mixed gas transportation for polymeric membranes are bound to experience (i) competition effect of mixed gas components, (ii) CO₂ plasticization, and (iii) membrane compaction. Competition effect observation occurred as number of components increased in feed gas that would result in reduction of components permeance as compared to single gas and binary gas system. Comparison of membrane performance in binary and mixed gas system have been evaluated using lab scale setup. It was found the membrane performance reduced from 5% to 10% when exposed from binary to mixed gas system (Fig. 6).

Plasticization and membrane compaction are interrelated phenomena when exposed to mixed gas containing CO₂ at elevated pressure. Plasticization can be either due to increase of CO₂ concentration or increased in feed pressure. Hypothetically, increasing CO₂ concentration would result in the increased of CO₂ permeance at reduced selectivity as depicted in Fig. 3. While, increasing feed pressure would lead to reduction of both CO₂ permeance and membrane selectivity as highlighted in Fig. 5.

Referring to Fig. 5, although the total membrane permeate flow is increased, the CO₂ permeance is reduced. This observation could be explained by the increased of other components permeation across the membrane other than CO₂ at elevated pressure. Thus, the CO₂ plasticization phenomenon is inevitable for polymeric membrane

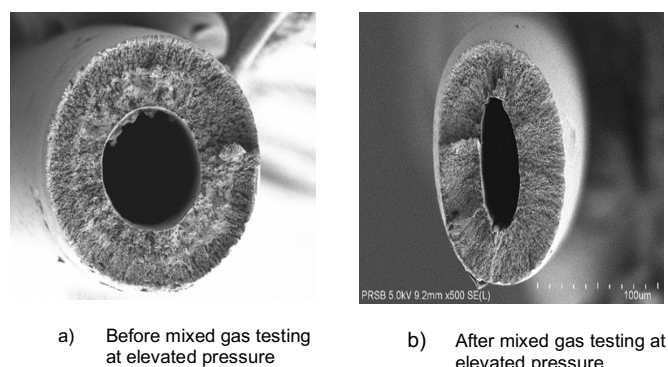


Fig. 8 Hollow fiber membrane cross section using FESEM.

Whereas for membrane compaction, the phenomenon could have resulted in (i) actual fiber to collapse and/or (ii) compaction of membrane transition layer. The fiber collapsing is illustrated in Fig. 8, as the fiber being exposed to feed gas pressure up to 60 barg for 40% CO₂ mixed gas. Although the fiber is physically collapsed, the total permeation is increased with respect to pressure increment. This would indicate the fiber is undergoing plasticization phenomenon hence increasing the hydrocarbon gases permeation across the membrane. Whereas, the compaction of membrane transition layer phenomenon has resulted in gradually reduction of fast gas permeation over period of timeline with insignificant reduction of membrane selectivity. In addition, as depicted in Fig. 7, the total membrane permeate flow is also reduced with respect to timeline.

Effect of permeate pressure

The membrane permeate pressures were varied from 0 barg to 4 barg to understand its consequences to membrane performance. As depicted in Fig. 9, the CO₂ permeance and membrane selectivity are gradually reduced with reduction of permeate pressure. However, the percentage reduction for membrane performance is insignificant (less than 10%) as compared to the feed gas pressure effect (more than 30%).

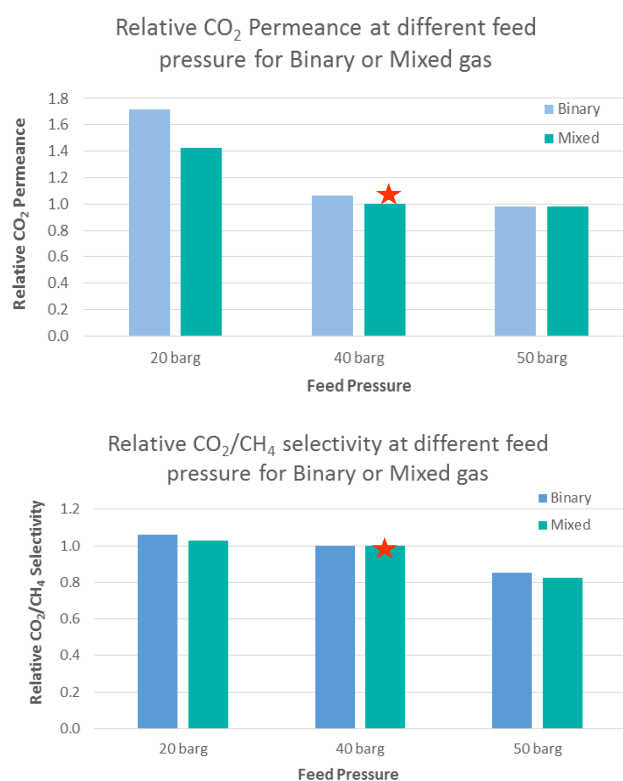


Fig. 6: Membrane performance for binary and mixed gas system. (★ = base value)

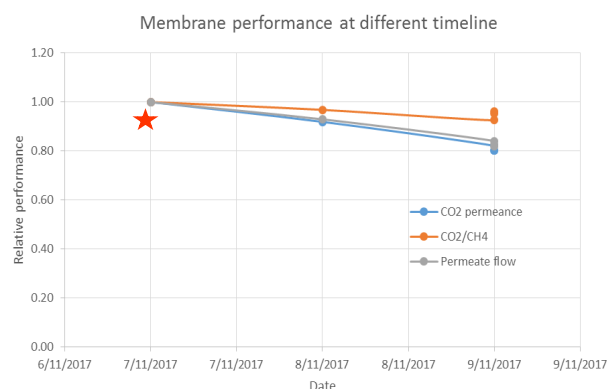


Fig. 7: Membrane performance at different timeline (★ = base value)

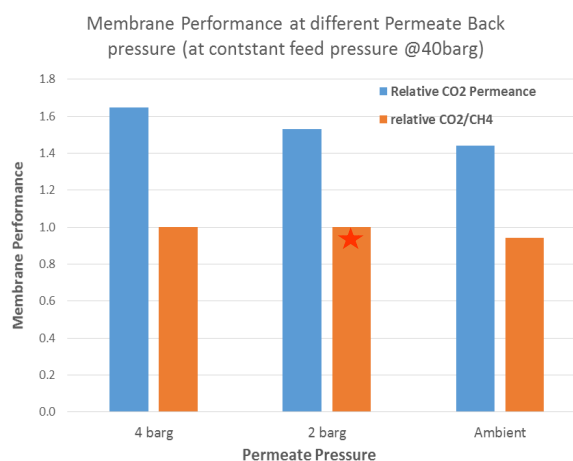


Figure 8: Membrane performance at difference permeate back pressure (★ = base value)

Conclusion

In summary, the membrane developed in this study demonstrates high pressure durability up to 50 barg with acceptable gas separation performance in the presence of high CO₂ feed gas (up to 70% CO₂). However, operating at 60 barg would be a challenge to the membrane since the separation performance is below the project target. In addition, the membrane developed could operate at temperature up to 55 °C with minimum impact to its membrane separation performance. In all cases, identifying the best operating flow rate is crucial since both CO₂ permeance and CO₂/CH₄ selectivity will be negatively impacted more than 20% if flow rate is below than the minimum target Reynolds number. In addition, further contaminants testing is necessary to evaluate the membrane performance in presence of contaminants. Moreover, the flow distribution study of the membrane module will be conducted in near future to further optimize the membrane performance. This work is crucial in developing the operational boundary of PETRONAS Membrane for technology development and deployment in monetizing high CO₂ gas field.

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