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# Application of catalytic membrane reactor for pure hydrogen production by flare gas recovery as a novel approach

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ABSTRACT

In the present study, application of catalytic membrane reactor as a novel approach for the flare gas recovery is proposed. A comprehensive two-dimensional non-isothermal model has been constructed to evaluate the performance of flare gas recovery process in the membrane reactor. The model is developed by taking into accounts the main chemical kinetics, heat and mass transfer phenomena and hydrogen permeation in the radial direction across a Pd–Ag membrane. The model predictions are validated based on different experimental results reported in literature. The impact of reactor operating conditions on the recovery process such as temperature and pressure, feed molar ratio and sweep gas ratio are investigated and discussed. The modeling results confirm that the flare gas conversion and hydrogen recovery improves with increasing the operating temperature, pressure and sweep ratio as a consequence of increasing the driving force for $H_2$ permeation through membrane. The environmental consideration revealed that by application of catalytic membrane reactor for the flare gas recovery of Asalouyeh gas processing plant (Iran), not only the equivalent mass of greenhouse gases emission reduces from 2179 kg/s to 36 kg/s, but also, 12.7 kg/s pure hydrogen will be produced by flare gas recovery at 750 K, 5 bar, sweep ratio of 5 and feed molar ratio of 4.



## Introduction

One of the most important section of GHGs emissions is related to gas flaring in the oil and gas industry [1,2]. In the gas flaring method, combustible components, mostly hydrocarbons of waste gases from industrial operational units, are burned via high–temperature oxidation process, and large amount of GHGs such as $CO_2$, nitrogen oxides ($NO_x$), sulfur oxides ($SO_x$), volatile organic compounds (VOC) and ozone are produced. The Global Gas Flaring Reduction Partnership (GGFR) today reported flaring data for 2017, indicating an overall increase in global flaring from the previous years. Recent assessment of satellite data revealed that more than 149 billion $m^3$ of associated gas was flared at the oil production sites across the world, an increase of 2 billion $m^3$ from 2015. This amount of global gas flaring is approximately equivalent to annual dispersion of 301 million tons of $CO_2$ into the atmosphere. Therefore, application of new technologies to avoid gas flaring and also waste gas burning in the flares is necessary to prevent and control the GHGs emission into the atmosphere. Different techniques such as Gas–to–Liquid (GTL) production, electricity generation with a gas turbine, compression and injection into refinery pipelines are

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proposed for flare gas recovery instead of conventional gas burning. In a related work, Zadakbar et al. [3] investigated the flare gases compression and recycling to the header for immediate use as a fuel. They reported that this method reduces the operating and maintenance costs, air pollution and GHGs emission, and fuel and steam consumption. Mourad et al. [4] considered the flare gas recovery through the crude oil stabilization process and suggested the utilization of this treated gas as a raw material for the petrochemical industry or compressed and re-injected into the reservoir in order to maintain the rate of oil production. Xu et al. [5] proposed a general methodology on flare minimization for chemical plant start-up operations via Plantwide Dynamic Simulation. In another related study, Rahimpour et al. [6] compared three different flare gas recovery techniques including gas–to–liquid (GTL) production, electricity generation via a gas turbine and flare gas compression and injection into refinery pipelines instead of conventional flare gas burning. Saidi et al. [7] and Siavashi et al. [8] evaluated the application of solid oxide fuel cell for the flare and purge gas recovery. In their approach, not only the emission of GHGs into the atmosphere is prevented, hydrogen is produced as a feed of fuel cell. Also, Abdulrahman et al. [9] investigations revealed that the clean development mechanism (CDM) can play an essential role in overcoming limitations facing the flare gas recovery projects in developing countries.

Hydrogen–based energy systems are introduced as an attractively alternative to common fossil fuel–based energy systems [10–13]. Energy conversion devices using hydrogen are highly efficient and produce very little or no harmful emissions. Therefore, there is a progressive interest for pure hydrogen production from waste gases and specially flare gas. Flare gas which contains mainly methane (80–95%), is one of the most interesting feed for hydrogen production via methane steam reforming (MSR). The main challenge of this process is related to $CO_2$ and CO production as well as hydrogen. In addition, it has such disadvantages as the conventional MSR process is equilibrium limited and requires elevated temperatures to achieve a high enough conversion of methane to be economically viable [14–17]. But high operating temperature destroys the catalysts structure and deteriorates its activity.

Application of hydrogen-selective membrane reactor as a novel technology can produce pure hydrogen with high conversion of methane [18,19]. Pure hydrogen production via MSR can be occurred by adding required steam to the flare gas in the catalytic membrane reactor (CMR). Pd and Pd–Ag based membrane reactors have been widely used because of their high permeability and selectivity towards hydrogen [20]. A significant enhancement in the methane conversion and process efficiency may be achieved by integrating reaction and separation in a single unit. Indeed, the continuous removal of hydrogen from the reaction zone of the membrane reactor allows overcoming equilibrium limitations to yield, and subsequently making it possible to take place the reaction at lower temperatures without decreasing process performance. Palladium–based thin wall is used extensively as hydrogen–permeable membrane in many reaction systems, due to its high permeability and selectivity, high resistance to temperature and corrosion.

In the present work, application of catalytic membrane reactor (CMR) as a novel approach for flare gas recovery of Asalouyeh gas processing plant is proposed. South–Pars gas field is the second largest reservoirs of natural gas in the world which is located in Iran. Asalouyeh gas processing plant is the biggest refinery in the south of Iran which has been constructed for the gas refining of South–Pars gas field. By considering environmental and economic limitations, and also due to enormous quantities of flare gas emission into the atmosphere from this plant, application of novel technologies to control and reduce the GHGs emission is necessary. The composition and conditions of the flare gas of Asalouyeh gas processing plant are reported in Tables 1 and 2 [21]. The main objective of the present study is to develop a clear understanding of the effects of various design and operating parameters on the flare gas conversion and also, $H_2$ recovery. In this novel approach, the sweetened flare gas is used as a feed of CMR to produce pure hydrogen, since the flare gas contains large amount of methane. The first step in this approach is flare gas sweetening process via removal of $H_2S$ from the gas and subsequently, hydrogen production via MSR process over Ni–$Al_2O_3$ catalyst. A two–dimensional non–isothermal stationary mathematical model is established to evaluate the behavior of the CMR performance for the flare gas recovery by taking into accounts the main chemical reactions, heat and mass transfer phenomena, where they play crucial role in the performance of process. The impact of different operating conditions on the process performance, including temperature (650–950 K), pressure (1–30 bar), sweep ratio (1–10) and feed molar ratio (2–8) is investigated.

## Sweetening process

Sweetening process is performed to remove $H_2S$ from the flare gas using a packed bed absorber column by amine solvents such as diethanolamine. As illustrated in Fig. 1, compressed flare gas is fed to the bottom of absorber column and the cooled lean amine solution is fed from the top of the column with counter–current operational mode. After absorption of $H_2S$ by the amine solvent, the sweet flare gas from the top of the absorber column enters to the CMR. Also, the acid–gas–rich–amine solution exits from the bottom of the column at an elevated temperature, due to the exothermic absorption reaction. After absorption process, the rich amine solution leaves the absorber and enters to a flash tank which operates at much lower pressure. In this step, any light–end hydrocarbons that are not captured in the absorber are removed and then the rich amine is sent to the lean/rich amine exchanger. Then the rich amine solution is sent to amine regenerator for

**Table 1 – Flare gas specification of Asalouyeh gas processing plant.**

| Specification | Value |
|---|---|
| Temperature (°C) | 34.19 |
| Pressure (kPa) | 305 |
| Molar flow (kgmol/h) | 17760 |
| Mass flow (kg/h) | 337600 |

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