

# Design and Analysis of a Process for Methane to Hydrogen Conversion Using Piston Reactor Technology

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The global demand for hydrogen is seeing significant growth mainly because it is a clean energy carrier. This work compares the piston reactor versus conventional flow reactor on the basis of hydrogen production via the partial oxidation route. A piston reactor is essentially a repurposed engine that is utilized as a reactor and is an emerging simple and compact technology. Advantages of piston reactors include high throughput, high temperature and pressure conditions at short residence times and rapid quenching steps. A process is synthesized and analyzed that implements the reactor for the partial oxidation of methane, including water-gas shift reactions and appropriate separation sequences to purify and maximize hydrogen production. The performance of the process is compared to that of a conventional partial oxidation process design. Results showed that the engine process results in higher hydrogen production costs compared to the conventional system. However, the piston reactor process has significant amounts of excess heat that could be applied for carbon dioxide capture and sequestration. Results showed that around 33 % lower CO<sub>2</sub> emissions could be achieved in the piston reactor process compared to conventional partial oxidation.

## 1. Introduction

The global demand for hydrogen is predicted to almost double by 2040, mainly because it is a clean energy carrier which can be produced from many renewable sources (International Energy Agency, 2020). This study investigates hydrogen production via methane partial oxidation using piston reactor technology. The piston reactor is an emerging concept that offers a simple, safe, and compact medium for chemical reactions (Ashok et al., 2021). While it is still in its early stage of development, the piston reactor is very similar to the traditional internal combustion engine. Conventional engines are utilized for power production by converting chemical energy in fuels to useful work. However, when used as piston reactors, the exhaust is the desired product. The crankshaft can be driven by an electric motor in the case of endothermic systems, or used to operate a generator in exothermic reactions. Piston reactors offer numerous advantages including high temperature and pressure conditions at short residence times, thereby enhancing the performance of a variety of chemical reactions. The cyclic series of reactant compression, heating, expansion, and rapid quenching steps offer a novel mode of carrying out chemical reactions. Moreover, the fast temperature quench allows the reactor to achieve a target non-equilibrium state where the desired product could be produced at optimal yield and efficiency (Ashok et al., 2021).

Process intensification is one of the most promising progress paths for developing more sustainable chemical processes through substantial improvement of equipment and process efficiency (Gerven and Stankiewicz, 2009). The application of piston reactor technology in chemical processes opens a new pathway for process intensification. Piston reactors have been studied for various applications including syngas production by methane or natural gas partial oxidation, steam methane reforming, nitric oxide production, and solid fuel partial oxidation (Lavrich et al., 2017). They have also been studied to synthesize ammonia, acetylene, sulphur, methanol, nanoparticles, amongst others. While piston reactors have been investigated in the literature, most of the published data have focused on its application for methane partial oxidation (POX) to syngas production (Ashok et al., 2021).

Cost assessment is a primary tool to pinpoint the most effective route for hydrogen production, and it will be particularly useful in process scaling up. To date, research reported in the literature focuses primarily on understanding the performance of the various piston reactor systems. There are limited techno-economic studies that assess the performance of chemical production processes that utilize such reactors (Ashok et al., 2021). To the authors' knowledge, there are only two reported techno-economic studies that incorporate such reactors, and both focus on small-scale application of natural gas conversion to methanol. Acocella et al. conducted a system and market analysis of compact engine reformers for the production of methanol. Results showed that small-scale conversion of natural gas to methanol in engine-based reformers is economically competitive (Acocella et al., 2014). Browne also performed a techno-economic analysis for the conversion of natural gas to methanol in an internal combustion engine as a micro-reformer, and assessed the environmental impact of the technology (Browne, 2019). To date, there are no techno-economic analyses on the application of piston reactors for hydrogen production. There is a gap in process design studies that integrate reactor engines with the necessary separation and energy-management to obtain cost-effective chemical production at various scale levels (Ashok et al., 2021). In this study, a conventional process for hydrogen production by methane partial oxidation is first developed. This serves as a benchmark for comparatively assessing the performance of a process implementing piston reactors.

## 2. Conventional methane partial oxidation process

A standard steady-state process for methane POX to hydrogen is designed as a benchmark for comparing the piston reactor-based process (Figure 1). Pre-heated methane and oxygen react in the POX reactor producing a syngas mixture comprising primarily of  $H_2$ , CO,  $CO_2$ . Required oxygen is produced in an air separation unit (ASU). While there are several air separation technologies, the most common commercialized method for producing pure oxygen are cryogenic processes (Smith & Klosek 2001). Since maximum hydrogen production is desired, the entire syngas stream is shifted to convert CO to  $H_2$ , followed by hydrogen separation and purification (Meyers, 2003). The WGS reactions occurs in two stages to obtain fast reactions and high conversions (Jakobsen and Åtland, 2016). The main technologies for hydrogen separation include adsorption, absorption, membranes and cryogenic processes (Voldsund et al., 2016). Over 85 % of current global hydrogen production processes employ pressure swing adsorption (PSA) technology (Liu et al., 2009). In this process, two PSA units are employed to increase hydrogen production. Tail gas from the PSA is treated in a catalytic incinerator to remove the remaining carbon monoxide and hydrogen, in addition to the unreacted methane. In a catalytic incinerator, catalysts enhance the combustion reaction rate, thereby requiring lower operating temperatures relative to thermal incinerators. This reduces the auxiliary fuel demand for waste-gas preheat, which ultimately lowers  $CO_2$  emissions (Baynham et al., 2017). A hydrogen production capacity of 500 t per day is selected as a large-scale base scenario. Optimum operating conditions presented in the literature are considered for the process's various units (Jakobsen and Åtland, 2016). Natural gas is assumed to be pure methane at 50 °C and 50 bar. In the reactor, high methane conversion (~97 %) is achieved, with a syngas  $H_2/CO$  ratio of ~1.9. Syngas leaving at 1,185 °C is cooled to 320 °C, and 190 °C before the HT-WGS and LT-WGS reactions, respectively. The PSA, operating at 23 bar and 25 °C, is modelled as a components splitter with 90 % recovery and 99.999 %  $H_2$  purity (Jakobsen and Åtland, 2016). The incinerator is designed following the approach presented in the EPA Air Pollution Control Cost Manual (Baynham et al., 2017). A summary of the main results can be found in Table 1. The flowsheet is simulated in AspenPlus using the HYSPLIT equation of state. The partial oxidation reactor is modelled as an adiabatic RGibbs reactor and WGS reactors are modelled as REquil. The air separation unit (ASU) is modelled using an input-output model with a power consumption of 0.35 kWh/ Nm<sup>3</sup> oxygen, to produce pure oxygen at atmospheric conditions (Jakobsen & Åtland 2016).

Since the heating and cooling utilities contribute to a substantial share to a process's operating costs, Heat Integration Pinch Analysis (Smith, 2008) is performed to maximize heat recovery within the system and generate electricity from process excess heat. Based on a minimum temperature difference of 10 °C, minimum heating and cooling demands are determined to be 0 and 144 MW, respectively. A heat exchanger network (HEN) is designed to meet the process's energy demands. Cooling duty is reduced by generating electric power using cogeneration, where excess heat from the process is extracted from the hot streams to generate high pressure steam in a condensing turbine. For maximum power production, very high pressure steam at 90 bar is generated (Shamsi and Omidkhah, 2012) and cooling water is used to satisfy the remaining cooling requirement. The total process power demand of 1.83 MWh/ t  $H_2$  produced, of which almost 50 % is needed in the ASU, are met using the power generated within the process, making the process self-sufficient in terms of both heating and power requirements.

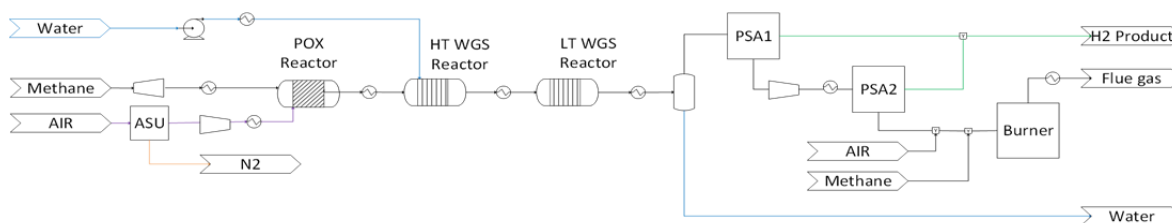


Figure 1: Overall process flowsheet for conventional methane partial oxidation reaction to hydrogen production

For the economic analysis, the capital and operating expenditures of the process are calculated for a plant lifetime of 20 y. These are then used to obtain a hydrogen production cost estimate for conventional methane POX. The percentage of delivered-equipment cost method is applied to obtain fixed-capital and total capital investments (Peters et al., 2003). Equipment costs are calculated using APEA and literature reference costs when applicable. HEN and reactor costs are estimated using correlations reported by Towler and Sinnott (Towler and Sinnott, 2008). The ASU and PSAs are costed based on data provided by Jakobsen and Atland (Jakobsen and Atland, 2016), whereas the incinerator is based on prices reported in the EPA cost manual (Baynham et al., 2017). Whenever necessary, the chemical engineering plant cost index is used to adjust costs and prices to 2018 US dollars, and capacity adjustments are applied using references from the literature (Jakobsen and Atland, 2016). Total CAPEX is annualized using the capital recovery factor, assuming an interest rate of 10 % (Keipi et al., 2018). A total specific CAPEX of \$417/ t hydrogen is determined from the analysis. Operating costs, consisting primarily of the feedstock requirements, cooling utility, and operational and maintenance costs, are also calculated. For a methane price of \$3.9/ MMBtu, total operating costs were found to be \$887/ t hydrogen. Considering both the CAPEX and OPEX, a hydrogen production cost of approximately \$1,304/ t hydrogen is obtained.

Table 1: Summary of the main results for conventional methane partial oxidation

Parameter	Unit	Value
H <sub>2</sub> produced (Plant capacity)	t per day	500
Methane demand	t CH <sub>4</sub> / t H <sub>2</sub>	2.9
Water demand (WGS)	t H <sub>2</sub> O/ t H <sub>2</sub>	6.6
Oxygen demand	t O <sub>2</sub> / t H <sub>2</sub>	3.1
CO <sub>2</sub> emitted	t CO <sub>2</sub> / t H <sub>2</sub>	8.2
Power demand	MWh/ t H <sub>2</sub>	0
Heating utilities	MWh/ t H <sub>2</sub>	0
CAPEX	\$/ t H <sub>2</sub>	417
OPEX	\$/ t H <sub>2</sub>	887
Hydrogen production cost	\$/ t H <sub>2</sub>	1,304

### 3. Piston reactor process description and analysis

A process flowsheet is developed around the piston reactor (Figure 2). Studies in the literature that have employed piston reactors for methane partial oxidation use air, rather than the pure oxygen used in the conventional process, as the oxidant (Ashok et al., 2021). Therefore, this process does not include an ASU, and air is fed directly into the piston reactor where it reacts with methane to produce syngas. After cooling and water separation, the syngas mixture is fed to a membrane system. Hydrogen is separated prior to the WGS reactions to shift the equilibrium in the right direction and enhance CO to hydrogen conversion, leading to a 10 % increase in hydrogen production. WGS reactions operate at temperatures similar to the conventional case. A membrane system is employed for the initial hydrogen separation, as it is a better suited technology for nitrogen-rich syngas. PSA is mainly intended for the treatment of streams with nitrogen concentrations that are below 5 % due to its relatively low affinity to most adsorbents (Delgado et al., 2015). WGS reactions are followed by another membrane separation step to recover the hydrogen generated in the reactors. Membrane systems typically produce hydrogen with a recovery and purity of 90 %. Therefore, to purify the hydrogen to similar conditions as the conventional case, a 2-step PSA process operating at 23 bar and 25 °C is included. The tail gas is mixed with the retentate of the membrane, pressure-reduced, and sent to the catalytic incinerator for treatment.

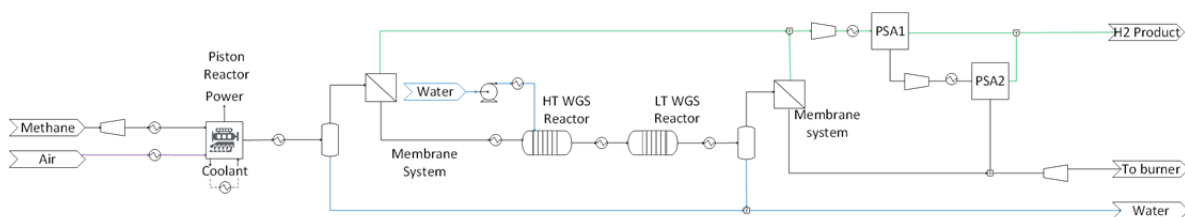


Figure 2: Process flowsheet design for hydrogen production using the piston reactor technology

A zero-dimensional single-zone model is developed to predict the performance of the piston reactor. The simulation consists of compression and expansion strokes, starting at the bottom dead center (BDC) with closed valves. A full rotation of the crankshaft is then carried out till the exhaust valve opening time. The model implemented corresponds to a single-cylinder piston reactor with a variable volume profile. It accounts for the time/crank angle change of volume, pressure, temperature, and species concentrations. A homogeneous gas mixture is assumed for each state; thus, spatial variations inside the piston chamber are not considered. The cylinder volume is calculated from the piston kinematics determined by the engine geometrical parameters, and the temperature is estimated from the conservation of energy applied to the cylinder volume (Gossler and Deutschmann, 2015). Heat losses through piston reactor walls are described using an empirical convective heat transfer correlation by Hohenberg (Hohenberg, 1979). In-cylinder pressure rise is calculated using a differentiated form of the ideal gas law with respect to time (Verhelst and Sheppard, 2009). The partial oxidation reaction kinetics is predicted using a combined reaction scheme for methane steam reforming by Xu and Froment (Xu and Froment, 1989) and complete methane combustion by Trimm and Lam (Trimm and Lam, 1980). Thermodynamic properties of the chemical species are represented by the seven-term NASA polynomials reported by Gordon and McBride (Gordon and McBride, 1994). The closed cycle model is discretized into small time steps. Then, a set of differential equations describing the mass and energy balances are solved simultaneously for each step using a built-in MATLAB ODE45 integrator. The simulated model is validated from a reference case developed by Hegner and Atakan, and the operating parameters are displayed in Table 2 (Hegner and Atakan, 2017). A fuel-rich feed consisting of 20.8 % CH<sub>4</sub>, 16.7 % O<sub>2</sub>, and 62.6 % N<sub>2</sub> is used. To quantify the energy released during the reaction, the total heat release is calculated, which is around 3.6 MWh/ t methane. This energy is divided into mechanical work, heat losses, and process heat with the effluent stream. The work output per cycle, the typical target output of such processes, is calculated by evaluating the area under the pressure-volume curve. The estimated work output is around 1.4 MWh/ t methane; thus, 38.8 % of the total energy generated by the reaction could be potentially transferred from the system as useful work, while around 0.9 MWh/ t methane is lost to the surrounding. The remaining energy exits the system with the hot exhaust gases. An input-output model is used to describe the piston reactor performance in the process simulation. The piston reactor process is designed for the same hydrogen production capacity as used for the above conventional process (500 t /day of final hydrogen product). The operating conditions of the WGS reactors, PSA units, and incinerator are modelled in the same manner as the conventional case, and the membrane process is simulated as a separation unit to capture the performance of an optimized membrane separation network consisting of two membrane separation stages with intermediate compression as reported by Mores et al. (Mores et al., 2018).

Table 2: Engine properties and parameters

Parameter	Specification	Exhaust composition	
Compression ratio	16.5:1	Component	mol %
Speed	3000 RPM	CH <sub>4</sub>	1.3
Intake pressure	1 bar	H <sub>2</sub>	22.9
Intake temperature	387 °C	H <sub>2</sub> O	8.7
Coolant temperature	127 °C	CO	12.9
Inlet methane/ air flowrates	2.4/ 16.2 kg/hr	CO <sub>2</sub>	2.9
Engine volume	425 cc	N <sub>2</sub>	51.3

The power generated from the engines and turbines are able to meet around 70 % of the total process power demand. The remaining 47 MW of power can be generated from excess process heat. The minimum heating and cooling demands of the process are determined to be 0 and 441 MW, respectively. A HEN is developed to integrate the process streams, and extra heating is used to generate steam to meet the power demands,

resulting in a self-supporting process. Cooling water is used to supply the remaining ~300 MW of cooling duty after steam generation. A techno-economic analysis approach similar to the one described in Section 2 is followed to obtain a hydrogen production cost estimate for the designed process. CAPEX values for the membranes and engines are obtained from the literature (Mores et al. 2018 and Browne 2019). Results showed that the total CAPEX and OPEX are \$1,620 and \$ 1,795/ t H<sub>2</sub>, respectively. This results in a hydrogen production cost of around \$3,415/ t H<sub>2</sub>. The results of the analysis are summarized in Table 3.

*Table 3: Main process results for hydrogen production by methane partial oxidation in piston reactors*

Parameter	Unit	Value
H <sub>2</sub> produced (Plant capacity)	t per day	500
Methane demand	t CH <sub>4</sub> / t H <sub>2</sub>	4
Water demand (WGS)	t H <sub>2</sub> O/ t H <sub>2</sub>	6.3
Oxygen demand	t O <sub>2</sub> / t H <sub>2</sub>	6.4
CO <sub>2</sub> emitted	t CO <sub>2</sub> / t H <sub>2</sub>	12.1
Power demand	MWh/ t H <sub>2</sub>	0
Heating utilities	MWh/ t H <sub>2</sub>	0
CAPEX	\$/ t H <sub>2</sub>	1,620
OPEX	\$/ t H <sub>2</sub>	1,795
Hydrogen production cost	\$/ t H <sub>2</sub>	3,415

#### 4. Comparison of process performances

Both processes are designed for the same hydrogen production capacity. They are also self-sufficient in terms of heating and power requirements. The piston reactor process uses more methane since, in addition to the lower methane conversion in the piston reactor, water is produced by hydrogen combustion. Larger feedstock requirements, coupled to the fact that the piston reactor operates on air rather than oxygen, result in a hydrogen production cost that is around 2.6 times more than the conventional process. Higher methane feed in the piston reactor also results in more CO<sub>2</sub> emissions than the conventional process. Unlike the conventional process, the piston reactor-based process has significant excess amounts of heat that could be utilized to capture and store some of the emitted carbon dioxide to lower the emissions. Literature reports that for a ton of CO<sub>2</sub> capture and sequestration (CCS), 250-300 kWh of electricity (Jackson and Brodal, 2019) and ~550 kWh of heat at 115 °C are required (Jakobsen and Åtland, 2016). Utilizing the excess heat available in the plant can be used to generate steam that runs through a back-pressure turbine to provide heat and power for CCS. This could potentially reduce the CO<sub>2</sub> emissions by ~54 %, resulting in 5.6 t CO<sub>2</sub>/ t H<sub>2</sub>. Compared to the base-case, 33 % less CO<sub>2</sub> emissions can be realized using process excess heat for carbon capture and storage.

When compared to water electrolysis with a specific energy consumption of 51.2 MWh/ t H<sub>2</sub>, the 5.6 t CO<sub>2</sub>/ t H<sub>2</sub> emissions produced from the piston reactor process after CCS would translate to 0.11 t CO<sub>2</sub>/ MWh. Such emissions are comparable to those from an electrolysis unit running on an electricity mix of around 25 % natural gas and 75 % renewables. This assumes CO<sub>2</sub> emissions of 0.41 and 0 t CO<sub>2</sub>/ MWh associated with electricity supplied from natural gas (Energy information Administration, 2020) and renewables, respectively.

#### 5. Conclusion

A process was designed embedding piston reactors for hydrogen production by methane partial oxidation. Standard steady state process design for methane partial oxidation was used as a benchmark for comparison. Heat Integration and economic analyses were conducted on both processes. Results showed that the piston reactor technology is not as competitive in terms of production cost. Limitations include the utilization of air, rather than oxygen, in the reactor, and the relatively lower methane conversion observed in piston reactors. However, the piston reactor process has significant amounts of excess heat that can be used to capture and store CO<sub>2</sub>, resulting in 33 % less emissions than the conventional process. Future work should evaluate emissions from piston reactor processes from a Life Cycle Analysis point of view. Moreover, given the importance of nitrogen separation in the overall economics of the partial oxidation process, further analyses should be done to explore piston reactor systems with more oxygen- enriched feeds. Future work also includes investigating the application of piston reactors for different hydrogen production routes (i.e. steam methane reforming), and other chemistries in order to establish the economic competitiveness of the technology. Future studies should also target exploring scale-effects with a focus on different degrees of modularization at unit and process levels, and their impact on economies of scale.

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