

## Article

# Parametric Study for Thermal and Catalytic Methane Pyrolysis for Hydrogen Production: Techno-Economic and Scenario Analysis

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**Abstract:** As many countries have tried to construct a hydrogen (H<sub>2</sub>) society to escape the conventional energy paradigm by using fossil fuels, methane pyrolysis (MP) has received a lot of attention owing to its ability to produce H<sub>2</sub> with no CO<sub>2</sub> emission. In this study, a techno-economic analysis including a process simulation, itemized cost estimation, and sensitivity and scenario analysis was conducted for the system of thermal-based and catalyst-based MP (TMP-S1 and CMP-S2), and the system with the additional H<sub>2</sub> production processes of carbon (C) gasification and water–gas shift (WGS) reaction (TMPG-S3 and CMPG-S4). Based on the technical performance expressed by H<sub>2</sub> and C production rate, the ratio of H<sub>2</sub> combusted to supply the heat required and the ratio of reactants for the gasifier (C, Air, and water (H<sub>2</sub>O)), unit H<sub>2</sub> production costs of USD 2.14, 3.66, 3.53, and 3.82 kgH<sub>2</sub><sup>-1</sup> from TMP-S1, CMP-S2, TMPG-S3, and CMPG-S4, respectively, were obtained at 40% H<sub>2</sub> combusted and a reactants ratio for C-Air-H<sub>2</sub>O of 1:1:2. Moreover, trends of unit H<sub>2</sub> production cost were obtained and key economic parameters of the MP reactor, reactant, and C selling price were represented by sensitivity analysis. In particular, economic competitiveness compared with commercialized H<sub>2</sub> production methods was reported in the scenario analysis for the H<sub>2</sub> production scale and C selling price.

**Keywords:** thermal methane pyrolysis; catalytic methane pyrolysis; H<sub>2</sub> production; process simulation; economic analysis; unit H<sub>2</sub> production cost



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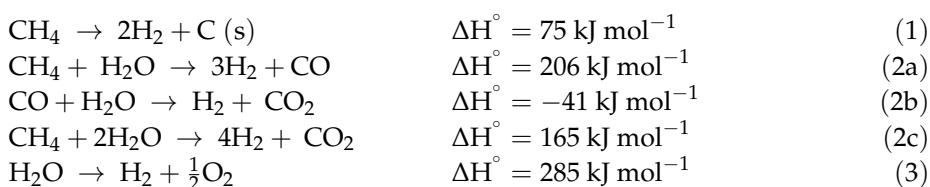
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## 1. Introduction

Many countries have tried to accomplish a successful transition of an energy system to hydrogen (H<sub>2</sub>) based on various political strategies such as ‘The National Hydrogen Strategy’ (2020) in Germany [1], ‘EU Hydrogen Strategy’ (2020) in the EU [2], ‘Basic Hydrogen Strategy’ (2017), ‘Strategic Energy Plan’ (2018), and ‘The Strategic Road Map for Hydrogen and Fuel Cells’ (2019) in Japan [3–5], ‘Hydrogen in a Low-carbon Economy’ (2018) in the UK [6], ‘H<sub>2</sub>@Scale’ (2021) in USA [7], and ‘National Hydrogen Roadmap’ (2018) in Australia [8]. These active approaches to an H<sub>2</sub>-based energy system come from the diverse advantages of H<sub>2</sub> as a clean energy carrier: it can be utilized in various energy sectors and easily combined in already constructed infrastructure, and, even though its volumetric energy density is relatively low, it shows a very high energy density of 120–142 MJ kg<sup>-1</sup> in the compressed state [9–15]. For the conventional production of H<sub>2</sub>, energy-intensive processes such as reforming, partial oxidation, and auto-thermal reforming of carbon-based fuels such as methane (CH<sub>4</sub>) and hydrocarbon have been mainly used. However, these conventional methods, including steam methane reforming (SMR), have led to negative environmental effects due to large emissions of carbon dioxide (CO<sub>2</sub>) [16–19]. Due to the

environmental issues of conventional methods, a lot of recent research has suggested water electrolysis (WE) powered by renewable energy as an alternative eco-friendly solution to produce H<sub>2</sub> because there is no CO<sub>2</sub> emission in the procedure [20–22]. However, there are still technical and economic challenges to be immediately utilized [23–25]; most H<sub>2</sub> production still depends on conventional methods with additional processes to reduce CO<sub>2</sub> such as SMR with CO<sub>2</sub> capture and storage (SMR with CCS) [26–28].

To overcome the limitations of current H<sub>2</sub> production methods, the concept of thermal methane pyrolysis (TMP), where H<sub>2</sub> and carbon (C) are directly produced in the gas phase (Equation (1)), has been paid attention as an alternative, novel H<sub>2</sub> production method owing to several technical, economic, and environmental benefits as follows: (a) there is no oxygen (O<sub>2</sub>) in the reaction leading to no CO<sub>2</sub> emissions or additional separation process, theoretically; (b) the process can be relatively simplified and lower energy is required than other methods such as reforming or partial oxidation; (c) reactant of the process, methane, is abundant and cheap leading to a cost effective operation of the process; (d) C products can be marketed because they are usually used as raw materials in various valuable materials such as rubber, tires, and pigments, etc.; (e) the separation of C is much easier than the separation of CO<sub>2</sub>; (f) it requires a lower amount of heat compared to SMR (Equation (2a–c)) and WE (Equation (3)), which are the most common and novel H<sub>2</sub> production methods (Equations (1)–(3)) [29–38].



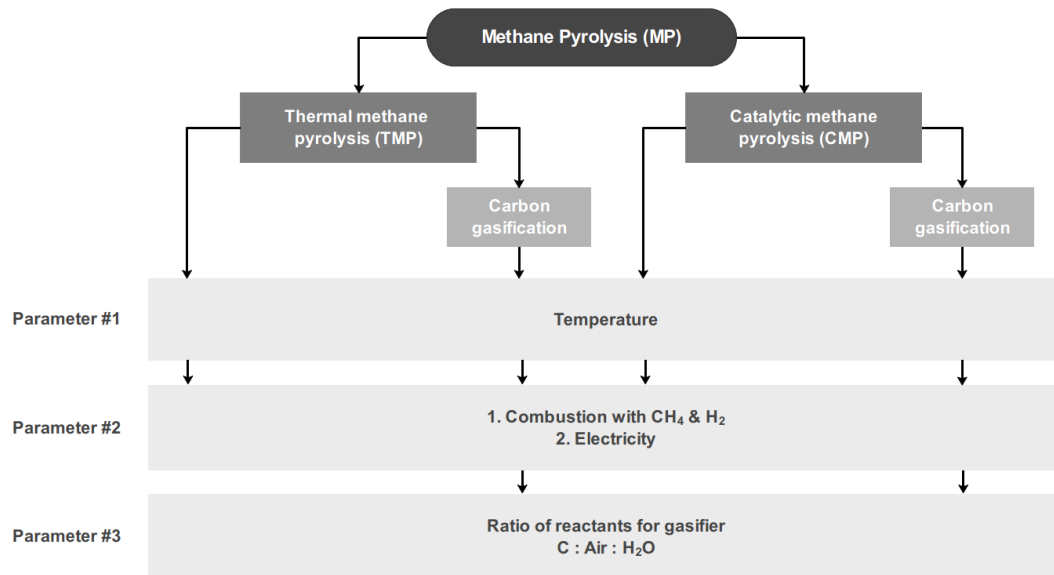
Because of its endothermicity and strong C–H bonding, TMP is usually operated at over 1373 K to obtain reasonable yields of H<sub>2</sub> and C leading to cost ineffectiveness and a large amount of energy being required [39,40]. These problems of having to use high temperature can be reduced by catalytic methane pyrolysis (CMP) where various types of catalysts (non-supported, metal supported, metal oxide supported, and carbonaceous, etc.) are adopted. Among the various catalysts used in CMP, the metal-based catalyst has very critical systematic limitations such as high toxicity of metal and rapid deactivation of the catalyst due to encapsulation of the active metal sites with C product [41]. Thus, carbon-based CMP has a lot of attention owing to the properties of carbon catalysts such as lower cost, higher stability, temperature resistance, and their ability to be safely stored due to their non-toxicity.

Based on the benefits of the concept of MP, many kinds of research have been conducted: Nishii et al. [42] carried out MP with different carbon-based catalysts (activated carbon, carbon black, mesoporous carbon, and carbon nanofiber) and found that all of these catalysts continued to maintain a CH<sub>4</sub> conversion of about 17% for longer than 600 min by catalyzing the produced C. It was reported that the produced C covered the catalyst surface, resulting in a specific surface area of 10 m<sup>2</sup> g<sup>−1</sup> and an intensity of D-Raman peak and G-Raman peak (I<sub>d</sub>/I<sub>g</sub>) from 1.5 to 1.57 irrespective of the original structures of C. Tezel et al. [43] designed an experiment using CMP with a calcium silicate-based Ni–Fe catalyst with different Fe loading by using the co-impregnation method. It was revealed that the addition of Fe can delay the deactivation of the Ni catalyst and an increase in the CH<sub>4</sub> flow rate can decrease the initial reactant conversion and lifetime of the catalyst. It was reported that the highest methane conversion of 69% is obtained at 973 K with the catalyst that has the highest Fe addition. Quan et al. [44] investigated the optimization of a fluidized bed reactor (FLBR) for CMP using 40 wt% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst, and catalyst activity and stability were investigated after optimization in terms of the catalyst bulk density, bed height, and particle size, etc. It was reported that the reaction conditions of 12 L (g<sub>cat</sub> h)<sup>−1</sup> feed dilution of 20% H<sub>2</sub>–CH<sub>4</sub>, and CO<sub>2</sub>-regeneration of deactivated catalysts are the best conditions for MP. Patzschke et al. [45] investigated promising catalysts for particle suspension in molten

NaBr-KBr and reported that mixed Co–Mn catalysts can be optimal candidates for methane pyrolysis in molten salts owing to their fast kinetics and stability. The authors reported that increasing the ratio of molar Co–Mn from 0 to 2 improved the conversion of CH<sub>4</sub> from 4.8% to 10.4% at 1273 K for the smallest catalyst particle size range, which shows that closeness between the catalytic surface and the gas phase can improve conversions. Karaismailoglu et al. [46] investigated the effect of the doping of yttria on a nickel catalyst synthesized by the sol–gel citrate method and reported CH<sub>4</sub> conversion of 50% with this type of catalyst. It was reported that the addition of Yttria can improve the stability and activity of catalysts at elevated temperatures and that a lower nickel ratio in the catalyst reduces the formation of carbon. Not only experimental studies but also systematic approaches using process simulations and works for economic feasibility have been reported. Chen et al. [47] designed the vacuum promoted methane decomposition with carbon separation (VPMDCS), which include a reactor of MP continuously generating H<sub>2</sub> and a C separation reactor converting carbon into CO. It was reported that VPMDCS showed CH<sub>4</sub> conversion of 99.2% and produced high-purity H<sub>2</sub> and CO with concentrations of both 99.6%. By economic analysis, the unit hydrogen cost of EUR 5.4 kg<sup>−1</sup> was reported. Riley et al. [48] simulated two concepts of CMP that used H<sub>2</sub> combustion and CH<sub>4</sub> combustion by Aspen Plus<sup>®</sup> comparing CO<sub>2</sub> emissions and H<sub>2</sub> production cost. It was revealed that the quality of produced C and its selling price are major factors in H<sub>2</sub> selling price, and H<sub>2</sub> production cost in the capacity of 216 ton d<sup>−1</sup> is less than USD 3.25 kgH<sub>2</sub><sup>−1</sup> without considering the sale of C. Perez et al. [49] designed an MP process using a quartz bubble column including molten gallium, which is used for catalyst and heat transfer agents, with a porous plate distributor. The authors found that a maximum CH<sub>4</sub> conversion of 91% was achieved at a reactor temperature of 1392 K where gallium occupied 43% of the total reactor volume with a residence time for a bubble of 0.5 s. Additionally, by techno-economic analysis, it was concluded that a molten metal system can be competitive with SMR if a CO<sub>2</sub> tax of EUR 50 ton<sup>−1</sup> is imposed and produced C is marketed. Kerscher et al. [50] designed two concepts of MP using electron beam plasma, which was generated from renewable electricity. The techno-economic assessment reported that levelized costs of H<sub>2</sub> for the electron beam plasma method ranged from 2.55 to 5.00 € kgH<sub>2</sub><sup>−1</sup>, and CO<sub>2</sub> emission ranged from 1.9 to 6.4 kgCO<sub>2</sub> eq. kgH<sub>2</sub><sup>−1</sup> from a carbon footprint assessment, which shows a high potential for reducing life cycle emissions. Zhang et al. [51] investigated the CO<sub>2</sub> mitigation costs of CMP and the integrated power generation process in a fuel cell comparing a combined-cycle gas turbine power plant system with and without CCS. It was revealed that CMP shows low life cycle emissions per unit of electricity output of 0.13 tCO<sub>2</sub> eq MWh<sup>−1</sup> but shows a high levelized cost of electricity of EUR 177 MWh<sup>−1</sup>, concluding that it has high potential when assumed that produced C can be sold at current prices. Timmerberg et al. [52] assessed the levelized hydrogen production costs and life cycle greenhouse gas (GHG) emissions from MP in three systems where molten metal, plasma, and thermal gas reactors were used. It was reported that the plasma-based system using electricity from renewable sources shows the lowest emissions of 43 gCO<sub>2</sub> MJ<sup>−1</sup>, and the molten metal and thermal gas system shows relatively higher GHG emissions due to the additional combustion and natural gas supply chain.

Even though many types of research have been conducted on the concepts of TMP and CMP, very few studies revealing both technical and economic viability of those technologies are reported, to the best of our knowledge. Therefore, in this study, a preliminary techno-economic parametric study is conducted to comprehensively investigate the feasibility of the concept of methane pyrolysis (MP). Firstly, a process simulation using Aspen Plus<sup>®</sup> for various MP processes, namely TMP and CMP, and with additional carbon gasification (TMPG and CMPG) are performed with detailed reaction kinetics under various technical parameters of reaction temperature, ratio of fuel combusted, and ratio of reactants for gasifier (C–Air–H<sub>2</sub>O) (Figure 1). Based on the technical performance from the process simulation, yields of H<sub>2</sub> and C, and the amount of fuel required to supply heat to the MP reactor and gasification unit are obtained, and then, economic feasibility in terms of unit H<sub>2</sub>

production cost is reported. In addition, to suggest future economic guidelines of this novel concept when this is commercialized, sensitivity and scenario analysis regarding various  $H_2$  production scales and different C selling price scenarios are conducted revealing the cost competitiveness compared to the conventional  $H_2$  production methods of SMR and SMR with CCS.

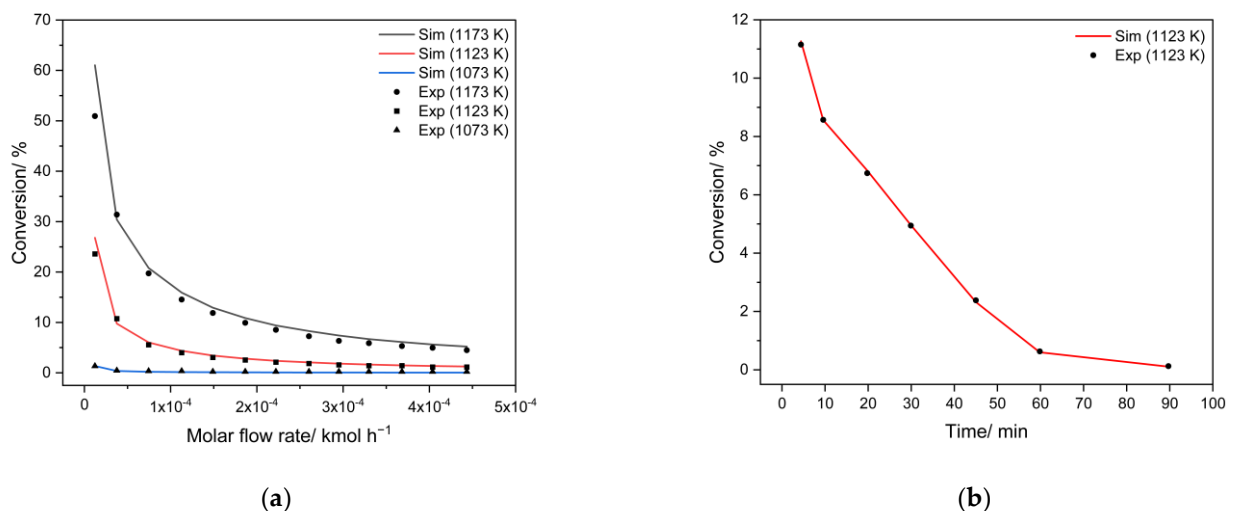


**Figure 1.** Schematic diagram of techno-economic parametric study for investigated systems for methane pyrolysis (MP).

## 2. Methods

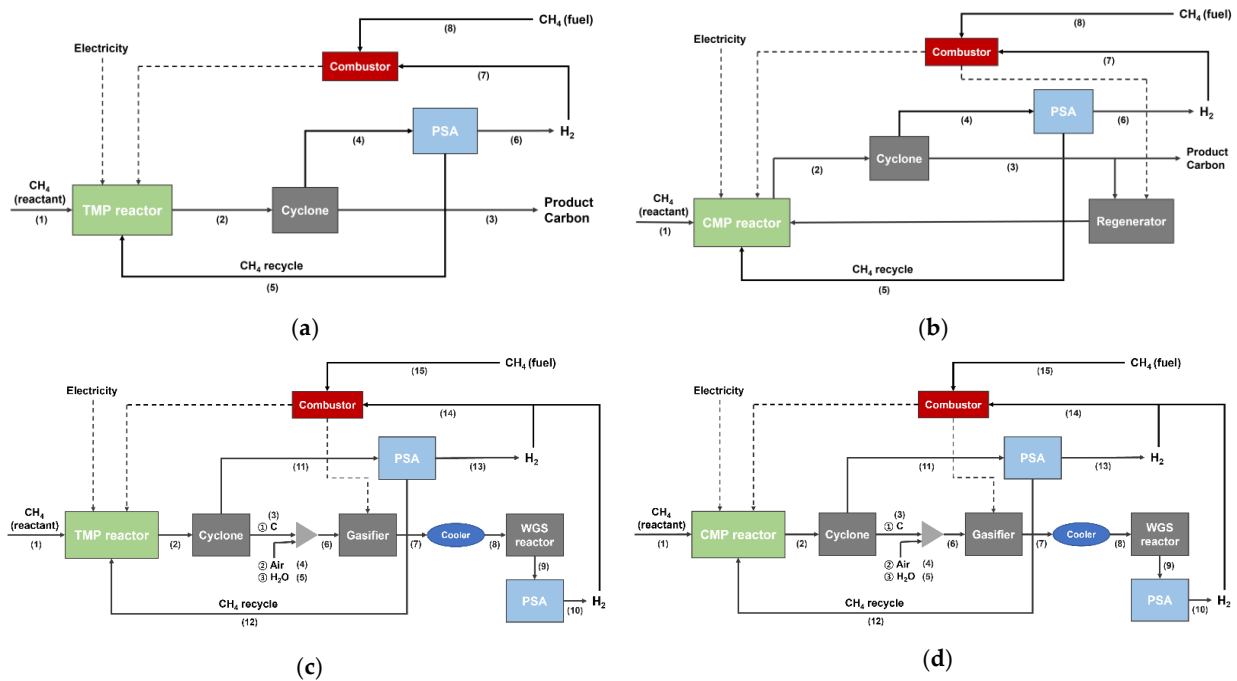
### 2.1. Process Simulation

In this study, four systems for MP, classified as TMP-S1, CMP-S2, TMPG-S3, and CMPG-S4, were simulated in Aspen Plus<sup>®</sup> (Aspen Technology, Inc., Bedford, MA, USA) with detailed reactor validation based on kinetics reported by Keipi et al. [53] for TMP and Kim et al. [54] for CMP. As a result, Figure 2 shows the closeness of methane conversion between experimental and simulated methods at each investigated operating conditions validating proper insertion of reported kinetics to Aspen Plus<sup>®</sup>.



**Figure 2.** Results of kinetic validation for (a) thermal methane pyrolysis (TMP) and (b) catalytic methane pyrolysis (CMP) reactions.

For all systems,  $\text{CH}_4$  entered the validated reactor in different temperature ranges of 1073–1373 K for TMP-S1 and TMPG-S3, and 1023–1173 K for CMP-S2 and CMPG-S4, then, product stream containing remained  $\text{CH}_4$  and produced  $\text{H}_2$  and C passed through the units of cyclone and pressure swing adsorption (PSA) for separating solid C and  $\text{H}_2$ , respectively (Figure 3). We assumed the pressure drop of cyclone as 0.01 bar and number of cyclones as only one and assumed separation efficiency of PSA as 100%. Especially for CMP-S2 and CMPG-S4, purified C entered the gasification unit to produce additional  $\text{H}_2$  and carbon monoxide (CO) with different ratios of C, air, and water ( $\text{H}_2\text{O}$ ) (1:1:1, 1:1:2, 1:1:3, 1:2:1, and 1:3:1), and water-gas shift (WGS) (Equation (2b)) reactor was followed to convert the produced CO to  $\text{H}_2$ . Additionally, for the heat supply system, various heat supply scenarios were assumed and classified as 100% electricity-based and different ratios of  $\text{H}_2$  combusted (0%–100% matched with 100%–0%  $\text{CH}_4$  combusted). Based on the result of the process simulation, material balance was obtained at the temperature of 1273 K for TMP-S1 and TMPG-S3 and 1173 K for CMP-S2 and CMPG-S4, with the ratio of  $\text{H}_2$  combusted of 40%, and the ratio of reactants for the gasifier of 1:1:2 (C-Air- $\text{H}_2\text{O}$ ) (Table 1).



**Figure 3.** Block flow diagrams for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4.

**Table 1.** Material balance for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
(a) TMP-S1								
Temperature/K	298	1273	1273	1273	1273	1273	1273	298
Pressure/bar	1.00	1.00	1.00	0.99	0.99	0.99	0.99	1.00
Molar flow/ $\text{kmol h}^{-1}$	1.00	3.02	1.00	2.02	0.02	2.00	0.27	0.12
Mole fraction								
$\text{CH}_4$	1.00	0.01	0	0.01	1.00	0	0	1.00
C	0	0.33	1.00	0	0	0	0	0
$\text{H}_2$	0	0.66	0	0.99	0	1.00	1.00	0

Table 1. Cont.

(b) CMPG-S2	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Temperature/K	298	1173	1173	1173	1173	1173	1173	298
Pressure/bar	1.00	1.00	1.00	0.99	0.99	0.99	0.99	1.00
Molar flow/kmol h <sup>-1</sup>	1.00	5.27	0.93	4.34	2.42	1.85	0.24	0.11
Mole fraction								
CH <sub>4</sub>	1.00	0.48	0	0.57	1.00	0	0	1.00
C	0	0.18	1.00	0	0	0	0	0
H <sub>2</sub>	0	0.35	0	0.43	0	1.00	1.00	0
(c) TMPG-S3	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Temperature/K	298	1273	1273	298	298	341	973	623
Pressure/bar	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Molar flow/kmol h <sup>-1</sup>	1.00	3.02	1.00	1.00	2.00	4.00	3.78	3.78
Mole fraction								
CH <sub>4</sub>	1.00	0.01	0	0	0	0	0	0
C	0	0.33	1.00	0	0	0.25	0	0
H <sub>2</sub>	0	0.66	0	0	0	0	0.30	0.30
O <sub>2</sub>	0	0	0	0.21	0	0.05	0	0
H <sub>2</sub> O	0	0	0	0	1.00	0.50	0.23	0.23
N <sub>2</sub>	0	0	0	0.79	0	0.20	0.21	0.21
CO <sub>2</sub>	0	0	0	0	0	0	0.15	0.15
CO	0	0	0	0	0	0	0.12	0.12
(c) TMPG-S3	(9)	(10)	(11)	(12)	(13)	(14)	(15)	
Temperature/K	623	623	1273	1273	1273	1273	298	
Pressure/bar	1.00	1.00	0.99	0.99	0.99	0.99	1.00	
Molar flow/kmol h <sup>-1</sup>	3.78	1.38	2.02	0.02	2.00	0.45	0.20	
Mole fraction								
CH <sub>4</sub>	0	0	0.01	1.00	0	0	1.00	
C	0	0	0	0	0	0	0	
H <sub>2</sub>	0.36	1.00	0.99	0	1.00	1.00	0	
O <sub>2</sub>	0	0	0	0	0	0	0	
H <sub>2</sub> O	0.16	0	0	0	0	0	0	
N <sub>2</sub>	0.21	0	0	0	0	0	0	
CO <sub>2</sub>	0.21	0	0	0	0	0	0	
CO	0.05	0	0	0	0	0	0	
(d) CMPG-S4	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Temperature/K	298	1173	1173	298	298	337	923	623
Pressure/bar	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Molar flow/kmol h <sup>-1</sup>	1.00	5.08	0.92	0.92	1.84	3.68	3.45	3.45
Mole fraction								
CH <sub>4</sub>	1.00	0.46	0	0	0	0	0	0
C	0	0.18	1.00	0	0	0.25	0	0
H <sub>2</sub>	0	0.36	0	0	0	0	0.30	0.30
O <sub>2</sub>	0	0	0	0.21	0	0.05	0	0
H <sub>2</sub> O	0	0	0	0	1.00	0.50	0.22	0.22
N <sub>2</sub>	0	0	0	0.79	0	0.20	0.21	0.21
CO <sub>2</sub>	0	0	0	0	0	0	0.16	0.16
CO	0	0	0	0	0	0	0.10	0.10
(d) CMPG-S4	(9)	(10)	(11)	(12)	(13)	(14)	(15)	
Temperature/K	623	623	1173	1173	1173	1173	298	
Pressure/bar	1.00	1.00	0.99	0.99	0.99	0.99	1.00	
Molar flow/kmol h <sup>-1</sup>	3.45	1.29	4.16	2.24	1.84	0.40	0.18	
Mole fraction								
CH <sub>4</sub>	0	0	0.56	1.00	0	0	1.00	
C	0	0	0	0	0	0	0	
H <sub>2</sub>	0.37	1.00	0.44	0	1.00	1.00	0	
O <sub>2</sub>	0	0	0	0	0	0	0	
H <sub>2</sub> O	0.15	0	0	0	0	0	0	
N <sub>2</sub>	0.21	0	0	0	0	0	0	
CO <sub>2</sub>	0.23	0	0	0	0	0	0	
CO	0.03	0	0	0	0	0	0	

## 2.2. Itemized Cost Estimation

To investigate the economic feasibility of each MP system, itemized cost estimation proposed by Turton et al. [55] was conducted considering various parameters of reaction temperature, types of fuel combusted and its ratio, and the ratio of reactant for gasifier. In this method, the unit H<sub>2</sub> production cost (USD kgH<sub>2</sub><sup>-1</sup>) is obtained from the sum of the total cost (USD y<sup>-1</sup>) divided by the total amount of H<sub>2</sub> produced (kg y<sup>-1</sup>). In this study, the total cost is defined as annualized capital cost (USD y<sup>-1</sup>), which is estimated from original



capital cost (USD) by applying capital recovery factor (CRF) as shown in Equation (4), and operating cost (USD  $y^{-1}$ ). Table 2 shows the list of these.

$$CRF = \frac{i(1+i)^N}{(1+i)^N - 1} \quad (4)$$

where  $i$  is a discount rate and  $N$  is an economic analysis period.

In addition, to properly estimate each capital cost, the six-tenth rule (Equation (5)) and concept of chemical engineering plant cost index (CEPCI) (Equation (6)) are applied to consider economics of scale and effects of inflation.

$$C_2 = C_1 \left( \frac{S_2}{S_1} \right)^{0.6} \quad (5)$$

where  $C$  is an equipment cost (USD) and  $S$  is a scale of the certain chemical process.

$$C_2 = C_1 \left( \frac{I_2}{I_1} \right) \quad (6)$$

where  $C$  is an equipment cost (USD) and  $I$  is a CEPCI.

**Table 2.** List of economic parameters and assumptions used in itemized cost estimation.

Economic Parameters	
Capital Cost	
MP reactor [56]	EUR 2740 k
WGS reactor [56]	EUR 59 k
Regenerator [57]	USD 12,112,138
Catalyst [58]	USD 1.138 $kg^{-1}$
Gasifier [56]	EUR 211 k
PSA [59]	$\frac{CEPCI}{392.6} \times 1,510,000 \times \left( \frac{\text{inlet flow rate}}{500} \right)^{0.6}$ (USD)
Cyclone [58]	USD 31,400
Supplement	20% of (Capital cost-Supplement) (USD)
Operating Cost	
CH <sub>4</sub> [60]	USD 0.005 $MJ_{LHV}^{-1}$
Catalyst operating cost	Assumed as 10% loss per month
Water [61]	USD 12 $ton^{-1}$
Electricity [32]	USD 56 $MWh^{-1}$
Labor [62]	USD 11 $hr^{-1}$
PSA operating cost [59]	$6.11 \times 100 \times (\text{inlet flow rate except } H_2)$ (USD)
C selling price [63]	EUR 500 $ton^{-1}$
Maintenance [64]	1% of (Capital cost-Supplement) (USD $y^{-1}$ )
Other cost [64]	2% of (Capital cost-Supplement) (USD $y^{-1}$ )
Economic Assumptions	
CEPCI (2021)	655.9
$i$	0.045
Exchange rate	USD 1 = EUR 0.85
$N$	20 years for MP reactor 10 years for WGS reactor, regenerator, PSA, PSA operating cost, cyclone, and supplement 1 year for catalyst
Stream factor	0.95

### 2.3. Sensitivity and Scenario Analysis

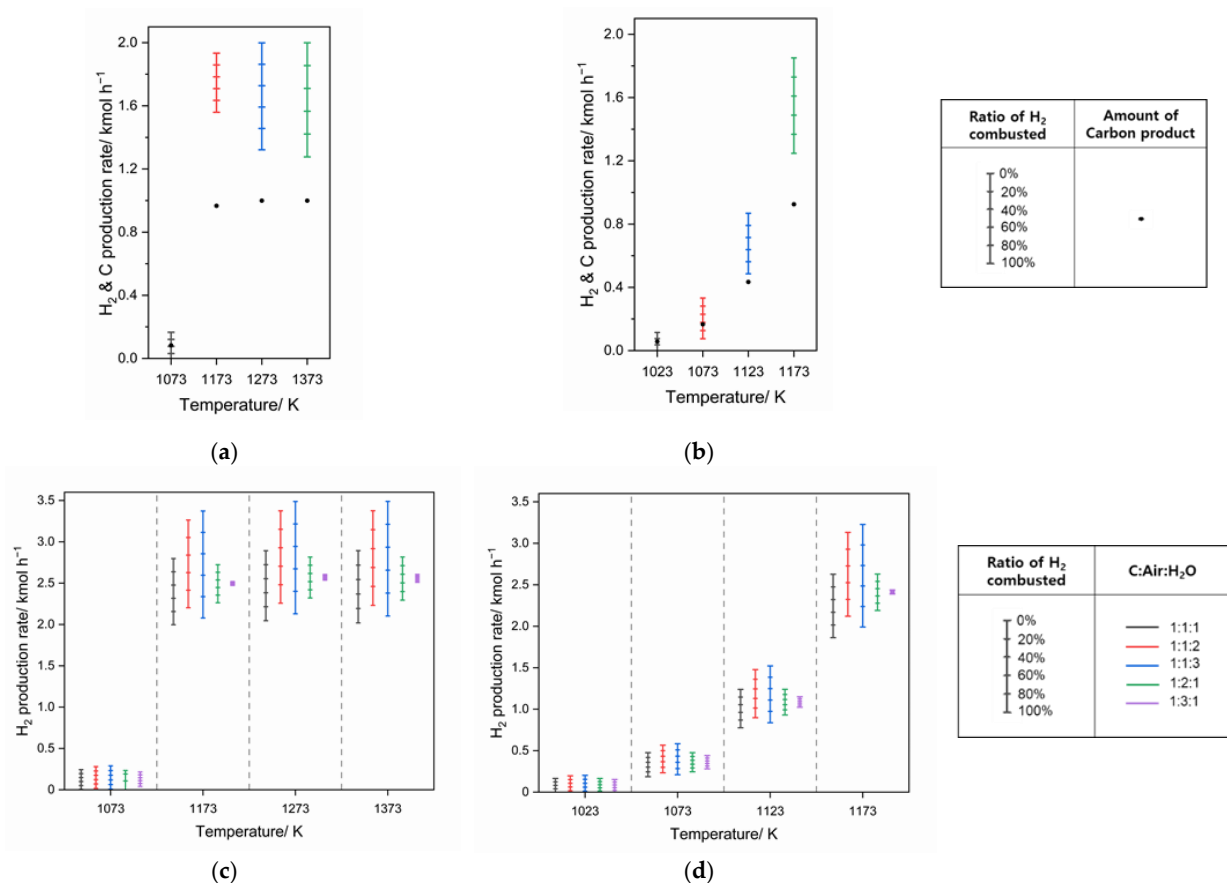
Key economic parameters of each system of MP and future unit H<sub>2</sub> production cost with varied C selling price, which can be advantages for economic feasibility, were quantita-

tively investigated by sensitivity and scenario analysis, respectively. For sensitivity analysis, with varied capital and operating cost in a range of  $\pm 20\%$  with other parameters fixed, the degree of variation in unit  $H_2$  production cost for each MP system was investigated. In addition, trends of unit  $H_2$  production cost for each scenario according to different  $H_2$  production scales and C selling prices were obtained and compared to conventional  $H_2$  production methods of SMR and SMR with CCS.

### 3. Results and Discussion

#### 3.1. $H_2$ and C Production Rates

Based on the result of the process simulation,  $H_2$  and C production rates for each MP system with a feed  $CH_4$  rate of  $1 \text{ kmol h}^{-1}$  were obtained at the different operating temperatures of 1073–1373 K for TMP-S1 and TMPG-S3 and 1023–1173 K for CMP-S2 and CMPG-S4, with the ratio of  $H_2$  combusted of 0%–100%, and the ratio of reactants composed of C, Air, and  $H_2O$  (Figure 4).



**Figure 4.** Technical performance for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4.

For TMP-S1 (Figure 4a), net  $H_2$  production rates of 0–0.17, 1.56–1.93, 1.32–2.00, and 1.28–2.00  $\text{kmol h}^{-1}$  and C production rates of 0.08, 0.97, 1.00, and 1.00  $\text{kmol h}^{-1}$  were obtained at a temperature of 1073 K, 1173 K, 1273 K, and 1373 K, respectively. As reaction temperature increased, the range of net  $H_2$  production rate was highly dependent on the ratio of  $H_2$  combusted due to the large amount of heat required and the different thermodynamic properties of each fuel, and produced C was maximized from 1173 K, not even the maximum investigated temperature.

For CMP-S2 (Figure 4b), 0.00–0.12, 0.08–0.33, 0.49–0.87, and 1.25–1.85  $\text{kmol h}^{-1}$  for net  $H_2$  production rates and 0.06, 0.17, 0.43, and 0.93  $\text{kmol h}^{-1}$  for C production rates were obtained at temperatures of 1023 K, 1073 K, 1123 K and 1173 K, respectively. Even though



an increasing trend of H<sub>2</sub> and C production rate and a high dependence of the ratio of H<sub>2</sub> combusted was shown, which are similar to the results from TMP-S1, no theoretical maximum amounts of H<sub>2</sub> and C (2 and 1 kmol h<sup>-1</sup>, respectively) were produced.

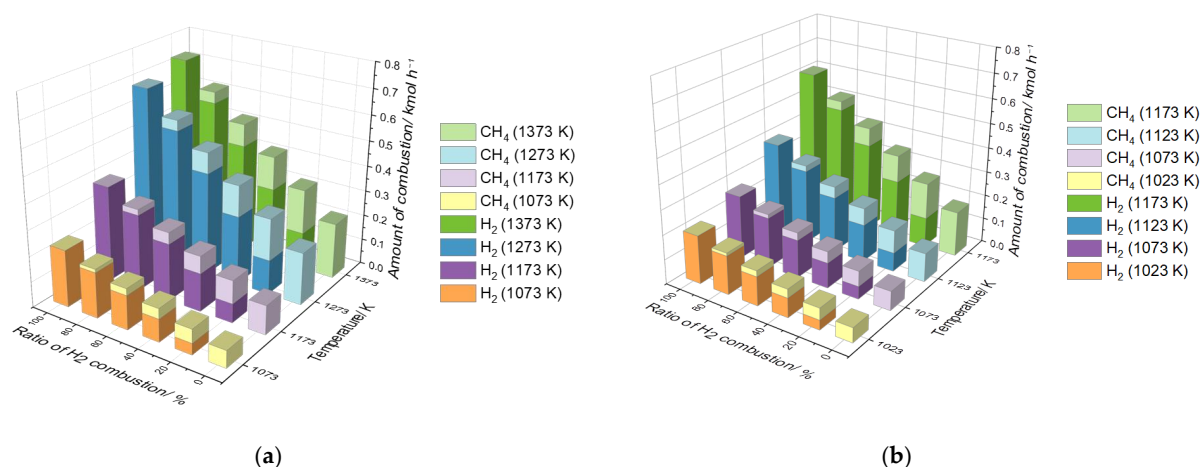
For TMPG-S3 (Figure 4c), even with the various ratios of C, Air, and H<sub>2</sub>O for the gasification unit, very low H<sub>2</sub> production rates of 0.00–0.29 kmol h<sup>-1</sup> were obtained at 1073 K. That poor technical performance, lower than the theoretical H<sub>2</sub> production rate of 2 kmol h<sup>-1</sup> for the previous system of TMP-S1, was raised by higher reaction temperatures of MP, leading to the improved technical performance of 2.00–3.49 kmol h<sup>-1</sup> H<sub>2</sub> production rates at 1173–1373 K. For the ratio of reactants in the gasifier, H<sub>2</sub> production rates at 1373 K dramatically increased 2.02–2.89 kmol h<sup>-1</sup> for a 1:1:1 ratio to rates of 2.10–3.49 kmol h<sup>-1</sup> for a ratio of 1:1:3, proving the importance of H<sub>2</sub>O in the additional H<sub>2</sub> production processes of C gasification and the WGS reactor. Compared to the effect of H<sub>2</sub>O on net H<sub>2</sub> production rates, an opposite effect of air was shown with decreased maximum H<sub>2</sub> production rates of 2.81 and 2.61 kmol h<sup>-1</sup> for the ratios of 1:2:1 and 1:3:1, respectively, down from 2.89 kmol h<sup>-1</sup> for a 1:1:1 ratio, thereby identifying its disadvantage in technical performance.

For CMPG-S4 (Figure 4d), lower H<sub>2</sub> production rates of 0.00–0.20, 0.19–0.58, and 0.78–1.52 kmol h<sup>-1</sup> were obtained than those from TMPG-S3 in a range of similar investigated temperatures (1073–1273 K). Even though the technical performance was improved at a higher reaction temperature of 1173 K showing H<sub>2</sub> production rates of 1.86–3.23 kmol h<sup>-1</sup>, this is still lower than those from TMPG-S3. For the effect of air and H<sub>2</sub>O on H<sub>2</sub> production rates, similar trends to those for TMPG-S3 of increased rates from 1.86–2.63 kmol h<sup>-1</sup> (1:1:1) to 1.99–3.23 kmol h<sup>-1</sup> (1:3:1) and decreased rates from 2.19–2.63 kmol h<sup>-1</sup> (1:2:1) to 2.39–2.44 kmol h<sup>-1</sup> (1:3:1).

As a result, through the trends of H<sub>2</sub> and C production rates obtained from the process simulation, the detailed effects of temperature, the ratio of H<sub>2</sub> combusted, and the ratio of reactants entering the gasifier were confirmed.

### 3.2. Parametric Study—Fuel Consumption

To investigate the amount of fuel combusted to cover the total heat required in each system, the required amount of fuel (H<sub>2</sub> and CH<sub>4</sub>) was obtained (Figures 5 and 6).

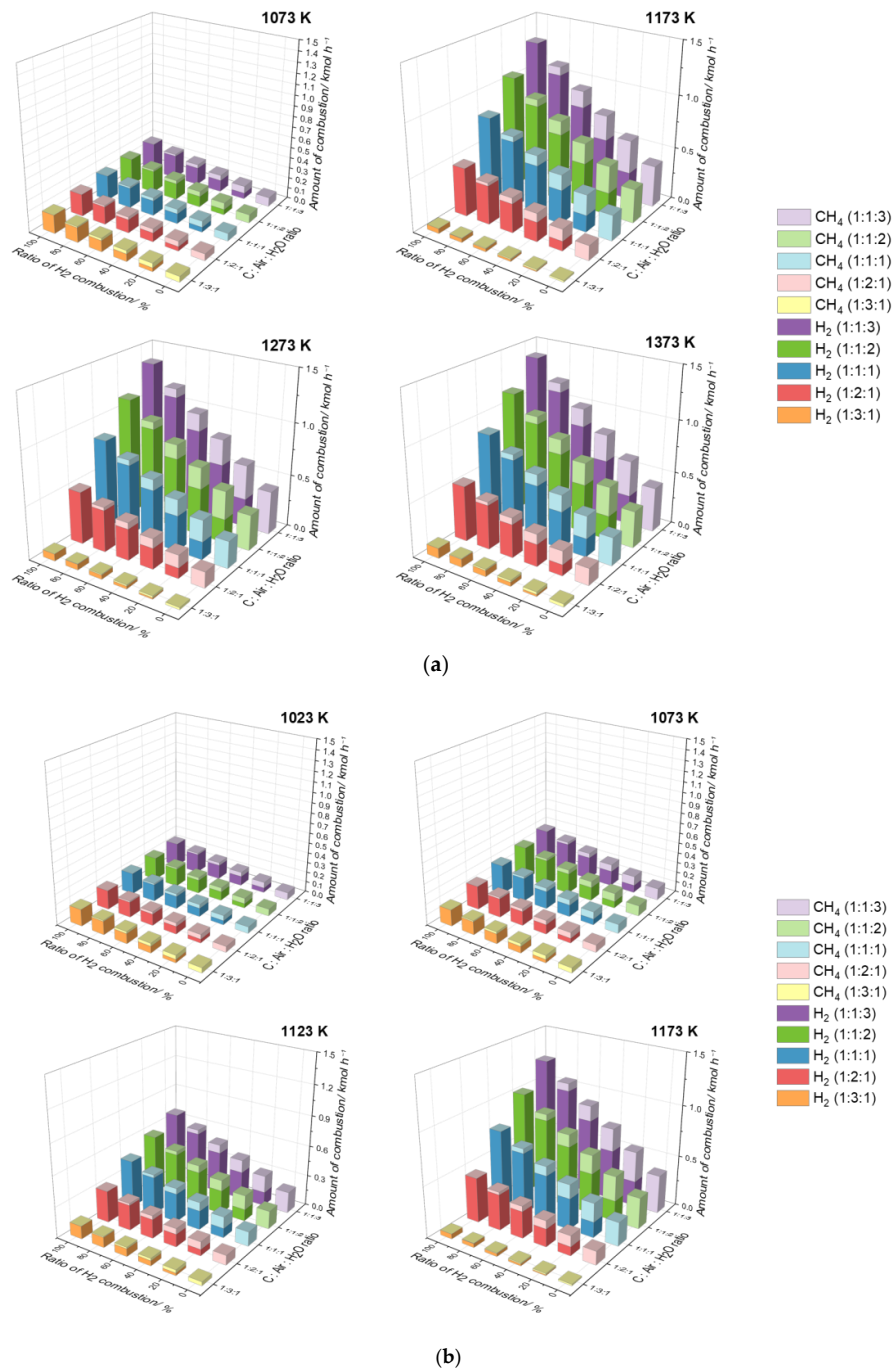


**Figure 5.** Amount of fuel (CH<sub>4</sub> and H<sub>2</sub>) consumption for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1) and (b) catalytic methane pyrolysis (CMP-S2) in temperature of 1073–1373 K and 1023–1173 K.

Figure 5 shows the required amount of fuel in TMP-S1 and CMP-S2 according to temperature and the ratio of H<sub>2</sub> combustion (0%, 20%, 40%, 60%, 80%, and 100%). From the process simulation, the total amount of heat required of 3425, 5739, 10,380, and 11,079 cal s<sup>-1</sup> for TMP-S1 were needed at 1073 K, 1173 K, 1273 K, and 1373 K, respectively, and that of 3016, 3941, 5868, and 9246 cal s<sup>-1</sup> for CMP-S2 were needed at 1023 K, 1073 K, 1123 K, and

1173 K, respectively, showing the higher amount of heat is needed for TMP-S1 than CMP-S2 due to its higher reaction temperature and the technical benefit of the catalyst-based MP.

For TMP-S1, the amounts of  $\text{CH}_4$  consumption were estimated as 0.07, 0.11, 0.21, and 0.22  $\text{kmol h}^{-1}$  and the amounts of  $\text{H}_2$  consumption of 0.22, 0.37, 0.67, and 0.72  $\text{kmol h}^{-1}$  were obtained when  $\text{CH}_4$  and  $\text{H}_2$  covered the total amount of heat required, respectively, showing an increasing trend as temperature increased. Similarly, for CMP-S2, 0.06–0.18  $\text{kmol h}^{-1}$  of  $\text{CH}_4$  consumption and 0.20–0.60  $\text{kmol h}^{-1}$  of  $\text{H}_2$  consumption were estimated when each type of fuel totally covered the required heat.



**Figure 6.** Amount of fuel ( $\text{CH}_4$  and  $\text{H}_2$ ) consumption for methane pyrolysis (MP) systems of thermal and catalytic methane pyrolysis with gasification and WGS reaction ((a) TMPG-S3 and (b) CMPG-S4) in temperature of 1073–1373 K and 1023–1173 K.

In Figure 6, the amount of required fuel to supply heat for TMPG-S3 and CMPG-S4 is shown. In TMPG-S3 and CMPG-S4, much larger amounts of heat of 2691–4330, 725–19852, 1047–20,821, and 1464–21,245 cal s<sup>-1</sup> for TMPG-S3 and 2503–3643, 2442–5737, 1925–10,514, and 745–18,954 cal s<sup>-1</sup> for CMPG-S4 were obtained as the temperature increased, showing much greater increase than previous systems due to the additional endothermic process of C gasification. For both systems in particular, the ratio of reactants of 1:1:3 showed the highest amount of heat required compared with other ratios due to its high reaction extent, represented by high H<sub>2</sub> and C production rates in Figure 4. In addition, the very high impact of H<sub>2</sub>O in the amount of heat required was confirmed again with trends of the required fuel at different ratios of reactants for the gasifier.

For TMPG-S3, the amount of CH<sub>4</sub> fuel required of 0.01–0.42 kmol h<sup>-1</sup> when it covers total heat required can be replaced by the amount of H<sub>2</sub> combusted of 0.05–1.39 kmol h<sup>-1</sup>; for CMPG-S4, the H<sub>2</sub> consumption range of 0.05–1.24 kmol h<sup>-1</sup> was estimated to replace the amount of CH<sub>4</sub> required of 0.01–0.37 kmol h<sup>-1</sup>.

### 3.3. Itemized Cost Estimation

Based on the results from the process simulation, the itemized cost estimation for each MP system using only CH<sub>4</sub> and H<sub>2</sub> as fuel was conducted to investigate unit H<sub>2</sub> production cost at the temperature of 1273 K for TMP-S1 and TMPG-S3 and 1173 K for CMP-S2 and CMPG-S4, with the ratio of H<sub>2</sub> combusted of 40%, and the ratio of reactants for the gasifier of 1:1:2 (C-Air-H<sub>2</sub>O) (Table 3).

**Table 3.** Results of itemized cost estimation for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4.

Items	(a) TMP-S1		(b) CMP-S2		(c) TMPG-S3		(d) CMPG-S4	
	Annualized Cost/USD y <sup>-1</sup>	Unit H <sub>2</sub> Production Cost/USD kgH <sub>2</sub> <sup>-1</sup>	Annualized Cost/USD y <sup>-1</sup>	Unit H <sub>2</sub> Production Cost/USD kgH <sub>2</sub> <sup>-1</sup>	Annualized Cost/USD y <sup>-1</sup>	Unit H <sub>2</sub> Production Cost/USD kgH <sub>2</sub> <sup>-1</sup>	Annualized Cost/USD y <sup>-1</sup>	Unit H <sub>2</sub> Production Cost/USD kgH <sub>2</sub> <sup>-1</sup>
1. Capital cost								
MP reactor	37,139	1.29	35,590	1.33	50,967	1.05	48,840	1.08
WGS reactor	-	-	-	-	1804	0.04	1729	0.04
Regenerator	-	-	19,233	0.72	-	-	-	-
Catalyst	-	-	6	0.00	-	-	6	0.00
Gasifier	-	-	-	-	6452	0.13	6183	0.14
PSA	11,323	0.39	17,924	0.67	21,320	0.44	25,460	0.56
Cyclone	224	0.01	214	0.01	224	0.00	213	0.00
Supplement	8833	0.31	11,665	0.44	13,819	0.28	13,854	0.31
2. Operating cost								
Reactant	33,704	1.17	33,704	1.26	33,704	0.69	33,704	0.74
Catalyst operating cost	-	-	6	0.00	-	-	6	0.00
Water	-	-	-	-	2448	0.05	2251	0.05
Fuel	4150	0.14	3696	0.14	6848	0.14	6189	0.14
Labor	7524	0.26	7524	0.28	7524	0.15	7524	0.17
PSA operating cost	2	0.00	183	0.01	178	0.00	341	0.01
Maintenance	11,489	0.40	15,173	0.57	17,975	0.37	18,021	0.40
Other costs	5745	0.20	7587	0.28	8988	0.18	9011	0.20
3. C selling price								
	-58,700	-2.04	-54,352	-2.03	-	-	-	-
4. Total cost								
	61,431	2.14	98,152	3.66	172,250	3.53	173,332	3.82

For TMP-S1, unit  $H_2$  production cost of  $USD\ 2.14\ kgH_2^{-1}$  was estimated considering the capital cost of the MP reactor, PSA, cyclone, and supplement, and the operating cost of reactant, fuel, labor, PSA operating cost, maintenance, and other costs. In this estimation, the costs of the MP reactor and reactant account for 31% and 28% of the production cost with no consideration of the C selling price ( $USD\ 4.17\ kgH_2^{-1}$ ), respectively, showing its high importance in the economic feasibility. For CMP-S2, unit  $H_2$  production cost of  $USD\ 3.66\ kgH_2^{-1}$  was estimated with additional items related to a catalyst such as the cost of the regenerator and catalyst, and its operating cost. Among economic parameters, it is clear that the costs of the MP reactor and reactant are the most influential economic factors, showing high ratios of 23% and 22% of the production cost without considering the C selling price ( $USD\ 5.69\ kgH_2^{-1}$ ). In both TMP-S1 and CMP-S2, where units of the gasifier and WGS reactor were not constructed in the process simulation, the cost of the MP reactor and reactant and the C selling price have a very high economic impact on  $H_2$  production.

For TMPG-S3 and CMPG-S4, additional economic parameters related to the gasification of C and the WGS reaction means that the costs of the WGS reactor, gasifier, and water were considered and compared to both TMP-S1 and CMP-S2. For both systems, the relatively increased unit  $H_2$  production costs of  $USD\ 3.53$  and  $3.82\ kgH_2^{-1}$  for TMPG-S3 and CMPG-S4, respectively, were estimated compared to those of  $USD\ 2.14$  and  $3.66\ kgH_2^{-1}$  for TMP-S1 and CMP-S2, respectively. In addition, similar to TMP-S1 and CMP-S2, costs of the MP reactor and reactant were found to be the most influential economic parameters showing portions of 30% and 19%, and 28% and 19% for TMPG-S3 and CMPG-S4, respectively.

Our results indicated that the selling of C can be a very effective way to obtain economic competitiveness through the concept of MP, and showed the importance of the cost of the MP reactor and reactant for economic feasibility.

### 3.4. Parametric Study—Economic Aspects

To investigate the effects of the important parameters of reaction temperature, the ratio of  $H_2$  combusted to supply the heat required in the process, and the ratio of reactants composed of C, Air, and  $H_2O$  for the gasifier on economic feasibility, a comprehensive parametric study revealing trends of unit  $H_2$  production cost was conducted (Figure 7).

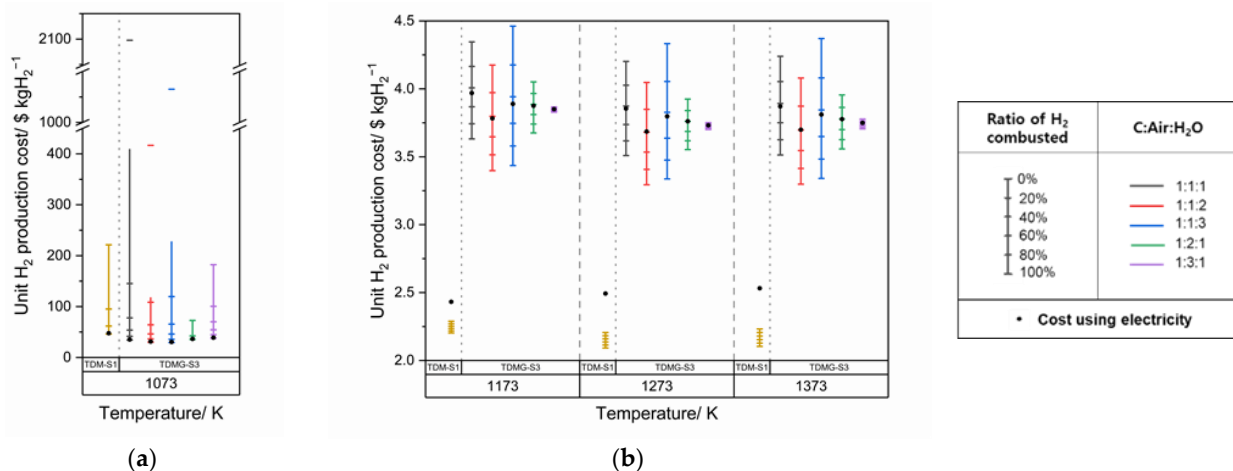
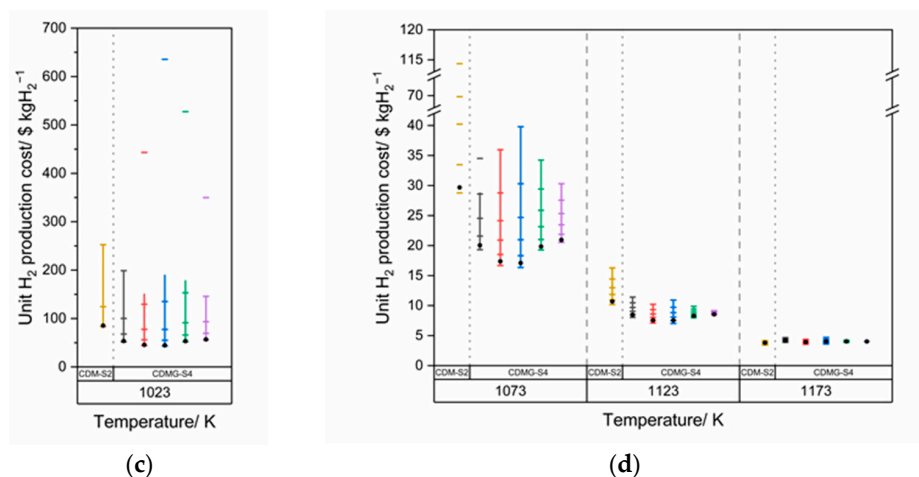


Figure 7. Cont.



**Figure 7.** Unit H<sub>2</sub> production cost for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and the systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4.

In the case of low temperature use where 1073 K for thermal-based systems (TMP-S1 and TMPG-S3) and 1023 K for catalyst-based systems (CMP-S2 and CMPG-S4) were considered, there were no economic benefits in either system. The minimum unit H<sub>2</sub> production costs of USD 46.09 kgH<sub>2</sub><sup>-1</sup> (TMP-S1) and USD 29.48–38.06 kgH<sub>2</sub><sup>-1</sup> (TMPG-S3) for thermal-based systems and USD 83.40 kgH<sub>2</sub><sup>-1</sup> (CMP-S2) and USD 43.11–55.56 kgH<sub>2</sub><sup>-1</sup> (CMPG-S4) for catalyst-based systems were reported. In addition, for the case of using electricity as the heat source, the cost was slightly higher but almost the same as the lowest cost using fuel combustion for both the thermal-based and catalyst-based system. Therefore, it is advantageous to use electricity as a heat source at low temperatures, but it still seems it would be difficult to gain economic benefits because of the high production costs.

In cases of high temperature, where 1173–1373 K for thermal-based systems and 1073–1173 K for catalyst-based systems were studied, cost reductions as temperature increased were shown. For TMP-S1, as temperature increased unit H<sub>2</sub> production costs of USD 2.20–2.29, 2.09–2.21, and 2.10–2.23 kgH<sub>2</sub><sup>-1</sup> and a cost reduction of 5.03% for each minimum cost were reported, which are much cheaper than the minimum costs for TMPG-S3 of USD 3.40, 3.29, and 3.30 kgH<sub>2</sub><sup>-1</sup>, proving the economic weakness of adopting the additional H<sub>2</sub> production processes of C gasification and WGS reaction. Interestingly, the lowest hydrogen production cost was found at temperatures of 1273K, even though it was not the highest temperature. In addition, for the case of using electricity, the cost for TMP-S1 is much higher at USD 2.43, 2.49, and 2.53 kgH<sub>2</sub><sup>-1</sup> than in the combustion case as temperature increased. However, in TMPG-S3, it shows values of USD 3.78–3.97, 3.69–3.86, and 3.70–3.87 kgH<sub>2</sub><sup>-1</sup> that are close to the average for combustion; thus, electricity can be beneficial as a heat source depending on the ratio of H<sub>2</sub> combusted.

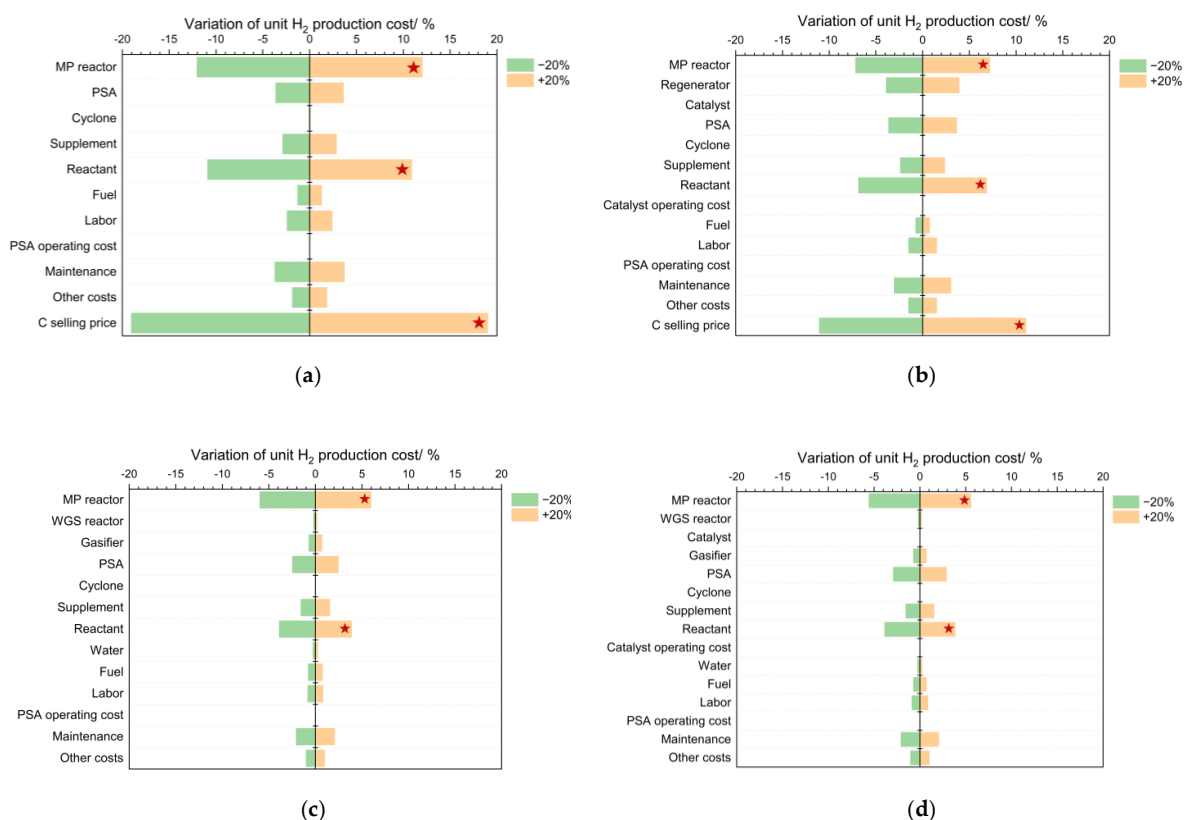
Compared to the trend of unit H<sub>2</sub> production cost for the thermal-based system, dramatic cost reductions in CMP-S2 were obtained for the catalyst-based system showing decreased unit H<sub>2</sub> production costs of USD 28.77–114.35, 10.17–16.28, 3.43–4.16 kgH<sub>2</sub><sup>-1</sup> due to its technical improvement as temperature increased. In addition, except at the temperature of 1173 K, the economic benefit of the processes for C gasification and WGS reaction was reported showing lower minimum unit H<sub>2</sub> production cost ranges of USD 16.34–20.52 and 7.02–8.42 kgH<sub>2</sub><sup>-1</sup> for CMPG-S4 than those of USD 28.77 and 10.17 kgH<sub>2</sub><sup>-1</sup> for CMP-S2 at 1073 K and 1123 K, respectively. In the case of electricity as the heat source, CMP-S2 shows costs of USD 29.68, 10.69, and 3.81 kgH<sub>2</sub><sup>-1</sup> and CMPG-S4 shows costs of USD 17.10–20.95, 7.55–8.55, and 3.93–4.20 kgH<sub>2</sub><sup>-1</sup> as temperature increased, showing slightly higher costs than the lowest cost using fuel combustion.

From these results, very critical effects, especially for the catalyst-based MP process, of temperature on economic feasibility and the need for the proper adoption of additional H<sub>2</sub> production processes can be revealed.



### 3.5. Sensitivity and Scenario Analysis

To investigate key economic parameters in each system and the possibility of the commercialization of each system, sensitivity and scenario analyses were conducted. In this study, one economic parameter was varied in the range of  $\pm 20\%$  with the remaining parameters fixed, and variations of unit  $H_2$  production cost for each system were obtained with key factors showing high variation remarked. Figure 8a,b reveal the economic importance of C selling price in both TMP-S1 and CMP-S2 showing very high variations of 19.1% and 11.1%, respectively. Costs of the MP reactor and reactant were also figured out as the next influential parameters showing variations of 12.1% and 10.9%, and 7.2% and 6.9% for TMPG-S3 and CMPG-S4, respectively. For TMPG-S3 and CMPG-S4, where all C is combusted leading to no profits from the selling of C, the same economic parameters of costs of the MP reactor and reactant were reported as the most influential factors with variations of 6.0% and 3.9%, and 5.6% and 3.9%, respectively (Figure 8c,d).

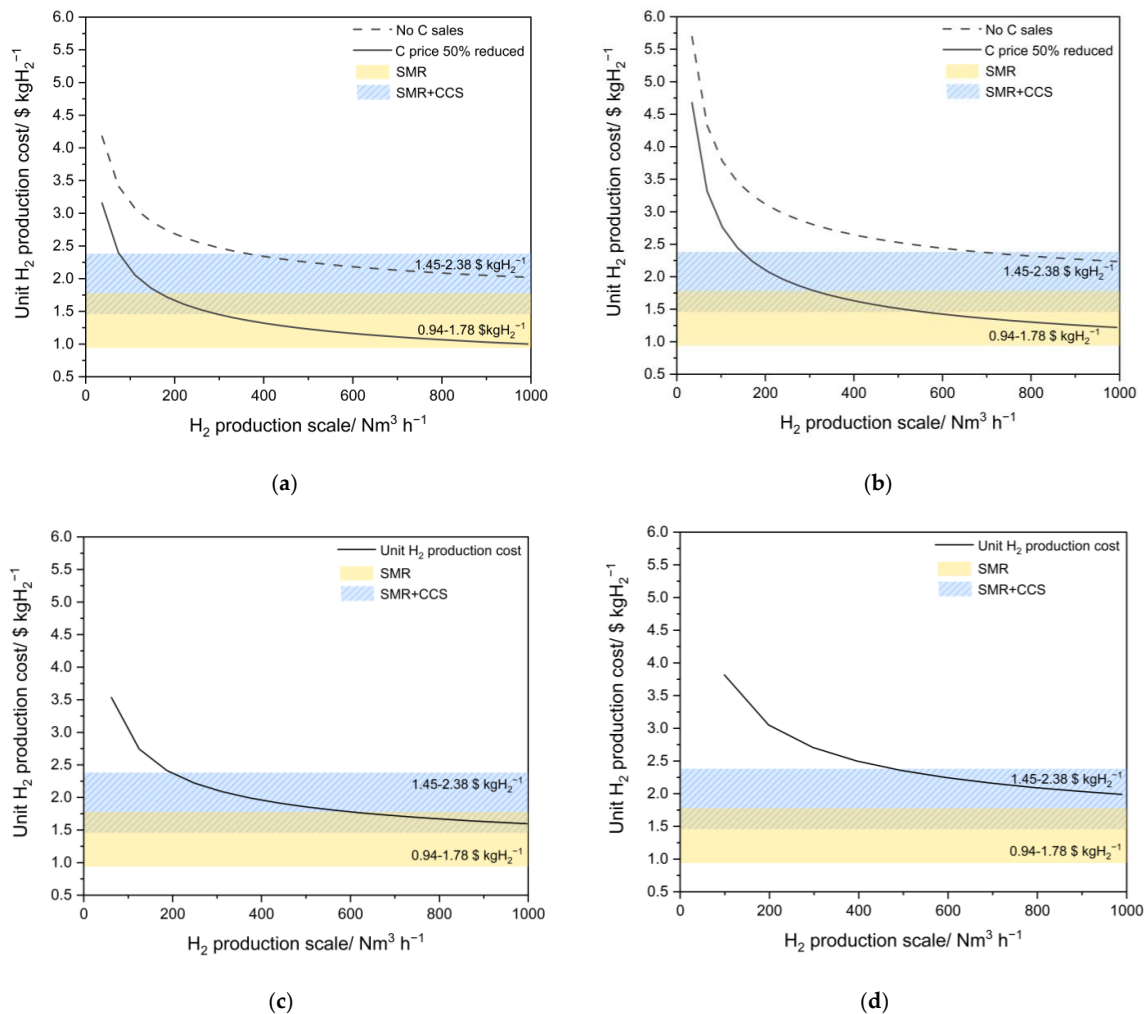


**Figure 8.** Results of sensitivity analysis for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and the systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4.

On the other hand, the scale of certain chemical engineering processes is also known to be a very influential factor to determine their economic feasibility [65]. Therefore, a scenario analysis for  $H_2$  production scale, which can lead to a cost reduction in capital cost as reported [66], and the different C selling price in the system of TMP-S1 and CMP-S2, which is a very crucial economic factor as reported by the sensitivity analysis, to reflect a pessimistic price fluctuation and low product quality of C, was conducted and compared to conventional  $H_2$  production methods of SMR (USD  $0.94\text{--}1.78\text{ kgH}_2^{-1}$ ) and SMR with CCS (USD  $1.45\text{--}2.38\text{ kgH}_2^{-1}$ ) [67] (Figure 9). As shown in Figure 9, there was a clear cost reduction as the  $H_2$  production scale increased due to the economics of scale. For CMPG-S4, unit  $H_2$  production cost decreased from USD  $3.82$  to  $1.99\text{ kgH}_2^{-1}$  ( $-47.9\%$ ) proving it can compete in price with SMR+CCS but not with SMR. Similarly, larger cost reductions of 51.6% and 60.7% were obtained for TMP-S1 and CMP-S2, respectively, with no C selling



price assumed (represented by USD 0  $\text{ton}^{-1}$ ), which are still not enough to compete with conventional  $\text{H}_2$  production methods of SMR.



**Figure 9.** Results of scenario analysis up to  $1000 \text{ Nm}^3 \text{ h}^{-1}$  for methane pyrolysis (MP) systems of (a) thermal methane pyrolysis (TMP-S1), (b) catalytic methane pyrolysis (CMP-S2), and the systems with additional gasification and WGS reaction of (c) TMPG-S3 and (d) CMPG-S4 with comparison to systems of steam methane reforming (SMR) of USD  $0.94\text{--}1.78 \text{ kgH}_2^{-1}$  and SMR with carbon capture and storage (CCS) of USD  $1.45\text{--}2.38 \text{ kgH}_2^{-1}$ .

However, for TMP-S1 and CMP-S2, with a C selling price of EUR  $250 \text{ ton}^{-1}$  ( $-50\%$  of the assumed C selling price) and for TMPG-S3, with unit  $\text{H}_2$  production costs decreased from USD  $3.16$  to  $1.00 \text{ kgH}_2^{-1}$ , USD  $4.68$  to  $1.22 \text{ kgH}_2^{-1}$ , and USD  $3.53$  to  $1.60 \text{ kgH}_2^{-1}$  showing reductions of  $68.3\%$ ,  $73.9\%$  and  $54.8\%$ , respectively, proving their economic competitiveness with conventional commercialized  $\text{H}_2$  production methods of SMR and SMR with CCS.

In short, the key economic parameters of C selling price and costs of MP reactor and reactant were calculated and the future economic competitiveness for all systems with high  $\text{H}_2$  production scales and C selling prices, even pessimistic prices, was confirmed.

#### 4. Conclusions

The promising alternative clean concept of  $\text{H}_2$  production of methane pyrolysis (MP) was technically and economically investigated by preliminary techno-economic analysis consisting of a process simulation using Aspen Plus<sup>®</sup>, itemized cost estimation, and sensitivity and scenario analysis for various parameters such as temperature, the ratio of fuel ( $\text{CH}_4$  and  $\text{H}_2$  produced from MP) combusted, and the ratio of reactants for C gasification

(C, Air, and H<sub>2</sub>O). To investigate various H<sub>2</sub> production scenarios, thermal and catalytic methane pyrolysis (TMP-S1 and CMP-S2) and systems with additional H<sub>2</sub> production processes composed of C gasification and WGS reaction (TMPG-S3 and CMPG-S4) were considered in this study. The results of the process simulation indicated that reaction temperature is the most influential process variable for determining the technical performance of all investigated systems, and catalyst-based MP (CMP-S2 and CMPG-S4) showed much lower net H<sub>2</sub> and C production rates than thermal-based systems (TMP-S1 and TMPG-S3), where theoretical maximum yields were obtained, due to different kinetics used in the simulation. In addition, the amount of H<sub>2</sub>O added in TMPG-S3 and CMPG-S4 was reported as the most important factor to increase the amount of H<sub>2</sub> produced. For an aspect of fuel consumption estimated from the amount of heat required for each system, trends similar to the net H<sub>2</sub> and C production were obtained showing the amounts of heat of 3425–11,079 cal s<sup>-1</sup> for TMP-S1, 3016–9246 cal s<sup>-1</sup> for CMP-S2, 725–21,245 cal s<sup>-1</sup> for TMPG-S3, and 744–18,945 cal s<sup>-1</sup> for CMPG-S4 matched with the required fuel amounts of 0.068–0.219, 0.060–0.183, 0.014–0.420, and 0.015–0.375 kmol h<sup>-1</sup> and 0.223–0.723, 0.197–0.603, 0.047–1.386, 0.049–1.236 kmol h<sup>-1</sup> for CH<sub>4</sub> and H<sub>2</sub>, respectively. From the itemized cost estimation for each system at 1273 K for TMP-S1 and TMPG-S3 and 1173 K for CMP-S2 and CMPG-S4, with 40% H<sub>2</sub> combusted, and the ratio of 1:1:2 for C-Air-H<sub>2</sub>O, unit H<sub>2</sub> production costs of USD 2.14, 3.66, 3.53, and 3.82 gH<sub>2</sub><sup>-1</sup> for each system, respectively, were obtained showing a very high portion of the costs of the MP reactor and reactant, and the economic benefits of the carbon (C) selling price. To investigate the effects of each parameter of temperature, the ratio of fuel combusted, and ratios of C, Air, and H<sub>2</sub>O on economic feasibility, a parametric study was conducted proving the economic benefits of high temperature and the additional H<sub>2</sub> production process of C gasification and WGS reaction for CMPG-S4 but not for thermal-based MP process. The importance of the costs of the MP reactor and reactant and the C selling price for economic feasibility was calculated again by sensitivity analysis, where the variation of ±20% was assumed, with variations of unit H<sub>2</sub> production cost of 19.1% and 11.1% for C selling price in TMP-S1 and CMP-S2, respectively, and 12.1%–5.6% and 10.9%–3.9% for costs of the MP reactor and reactant, respectively, in all investigated systems. In addition, the effects of H<sub>2</sub> production scale for all systems and the C selling price for TMP-S1 and CMP-S2 on the unit H<sub>2</sub> production costs were investigated suggesting that all systems can compete with SMR with CCS, and especially TMP-S1 and CMP-S2, even with the pessimistic 50% reduced C selling price; for TMPG-S3, economic competitiveness with the commercialized H<sub>2</sub> production method of SMR can be achieved when an H<sub>2</sub> production scale larger than 1000 Nm<sup>3</sup> h<sup>-1</sup> is assumed.

Conclusively, the techno-economic feasibility of MP processes, classified as the four systems of TMP-S1, CMP-S2, TMPG-S3, and CMPG-S4, was investigated with detailed H<sub>2</sub> and C production rates, the amount of fuel required to supply heat in each system, the trends of unit H<sub>2</sub> production cost according to temperature, the ratio of H<sub>2</sub> combusted, and the ratio of reactants used in the C gasifier, and revealed key economic parameters of the costs of the MP reactor and reactant and the C selling price. Although several techno-economic enhancements such as scale-up should be researched further to accomplish the economic competitiveness of MP compared to SMR, the environmental benefits of MP are clearly shown in this study based on its theoretical reaction stoichiometry and trends of its consumption of fuels. Based on the results, the potential of both thermal and catalytic MP for promising H<sub>2</sub> production is clearly presented.

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## Nomenclature

CO <sub>2</sub>	Carbon dioxide
CO	Carbon monoxide
CCS	Carbon capture and storage
CMP	Catalytic methane pyrolysis
CMPG	Catalytic methane pyrolysis with carbon gasification
CRF	Capital recovery factor
CEPCI	Chemical engineering plant cost index
MP	Methane pyrolysis
FLBR	Fluidized bed reactor
GHG	Greenhouse gas
H <sub>2</sub>	Hydrogen
CH <sub>4</sub>	Methane
PSA	Pressure swing adsorption
SMR	Steam methane reforming
SMR with CCS	Steam methane reforming with carbon capture and storage
TMP	Thermal methane pyrolysis
TMPG	Thermal methane pyrolysis with carbon gasification
VPMDCS	Vacuum promote methane decomposition with carbon separation
H <sub>2</sub> O	Water
WE	Water electrolysis
WGS	Water-gas shift

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