Simulation of Hydrogen Production from Dry Reforming of Methane Based in Micro-reaction Technology

María Córdoba^{*}, Esmeralda Portillo, and Benito Navarrete

Chemical and Environmental Engineering Department, School of Engineering, University of Seville, Seville, Spain Email: marcorrod@alum.us.es (M.C.); eportillo@us.es (E.P.); bnavarrete@us.es (B.N.)

*Corresponding author

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Abstract—The performance and viability of Dry Reforming (DR) are important from an environmental perspective due to the increasing problem of Greenhouse Gases (GHGs) emissions, such as carbon dioxide and methane. This work aims to study an industrial plant based in this mechanism whose reaction consumes two GHGs to produce syngas, the most demanded intermediate product. Similarly, an energy integrated plant scheme is design to avoid the consumption of auxiliary currents using simulation tools such as Aspen Plus®. Different operating temperature scenarios and configurations are suggested to identify the optimal conditions to achieve maximum production. The technologies studied for DR reaction is the micro-reaction technology, as it allows to perform industrial reactions in minimal space. Finally, a validation of the model was carried out with experimental data, determining the accuracy of the results obtained.

Keywords—dry reforming, hydrogen, micro-reaction, circular economy

I. INTRODUCTION

Currently, one of the most important challenges is the reduction of Greenhouse Gases (GHGs) and climate change, which cause the global average temperature to increase up to 1.5 °C [1]. This is a result of the constant and accelerating emission of carbon dioxide, which the majority is due to the combustion of fossils fuels and industrial activity [2, 3].

Under these circumstances, it is proposed to valorise this GHG to avoid it emission. The objective of this work is to convert carbon dioxide and methane in a useful primary material. Thus, it is an exceptional opportunity to integrate CO_2 in a circular economy [4–6].

At this time, there are multiple existing technologies including: supercritical CO_2 as a reactive solvent, production of fuels or chemicals by catalytic, electrochemical and bioconversion, CO_2 copolymerization and CO_2 carbonation [4, 6]. This last-mentioned technology, also called mineral carbonation, is one of the most advanced and commercialized processes [4] but, it has a high compression and liquefaction cost.

While keeping the main focus on a circular economy, it should be noted that catalytic conversion, as highlighted in Fig. 1, has been subject of increasing attention over the years. This is particularly the case for Dry Reforming of Methane (DRM) [7].

Even though this technology development lies between laboratory scale and executed in a relevant environment [TRL (Technology Readiness Level) 4–6], it is considered a potential environmentally friendly technology [8]. This is due to the mechanism, as it consumes two GHGs to produce syngas, a mixture of hydrogen and carbon monoxide (1).



Fig. 1. Publications and citations related to dry reforming from 1989 to 2023 [9].

Syngas, also known as synthesis gas, is a significant intermediate product due to its essential role in the production of others important compounds: ammonia, methanol, gas-to-liquids, among others. The annual production is about 6 EJ per year [10].

Strong deactivation of the catalyst due to coke formation is one of the higher problems faced and the main reason why there is no further large-scale production [11]. To avoid this problem, there has been lots of reactor configurations studied. One of them is the microreactors, first considered in 1960 as an alternative to conventional reactor [12]. In 1995, the first study of microsystem technologies for chemical and biological microreactors was produced in Germany [12].

This structure and reduced size can avoid coke formation and cold/hot spots [13]. Even, it allows a better contact between catalyst and reactive as it can be structurally design [13]. Microreactors can be fabricated using a wide range of materials: polymers, silicon, metal, ceramics, etc. [14].

In this case, two types of monoliths have been compared: a ceramic monolith with a gyroid structure and a metallic monolith manufactured with parallel channels.

Others benefits from microreactor technology is a significative reduction of the thermal energy, as it has a reduced size and can be easily isolated [7, 12–14].

This fulfils the aim of developing an environmentally friendly technology and global decarbonization. To help this purpose, the use of biomass and its gasses as a reactive is another key. This is referred to organic, non-fossilized and biodegradable substances originated from plants, animals and microorganisms [15]. From biomass decomposition emerges biogas, a methane-rich and inexpensive gas (4.4 USD/GJ) [16]. This gas meets every necessity and objective expressed in this introduction, so it is the one used in experimental procedure and simulation.

 $CO_2(g) + CH_4(g) \rightarrow 2CO(g) + 2H_2(g) \Delta H^0_r = 247.3 \text{ kJ/kmol}$ (1)

As mentioned before, the main problematic relies in coke formation and endothermic nature of the reaction. This is reflected in the majority of the studies around DRM, that are mostly about catalyst development due to the problems mentioned. This can be easily solved with micro-reaction engineering, so it is proposed to reproduce a DRM industrial scale plant based in microengineering. Another objective is to search for the optimal energetic integration between process streams through Aspen Plus. This tool provides mass and energy balance of the whole plant.

The main reactor is a 3D printed ceramic microreactor and a metallic microreactor with parallel channels, whose chemical activities have been studied in previous works [17, 18] respectively. The main catalyst configuration is Rh/Al₂O₃, as is the one studied in the references described. Seemingly, this is supplemented with a Water-Gas-Shift section (WGS) (2), reforming the produced carbon monoxide with water. This increases the hydrogen production and heat utilisation, as this reaction is performed at high temperatures [19].

$$CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$$
⁽²⁾

II. MATERIALS AND METHODS

A. Simulation and Data Input

The simulation model was developed through Aspen Plus V.8.8 software, considering a laboratory scale, processing a 6.678 Nm^3/h biogas steam and 7.207 Nm^3/h of water with compositions expressed in Table 1 [19].

Table 1. Molar composition of the reactants considered in the simulation [19]

			[-/]		
Depative -	Molar fraction				
Reactive -	CH ₄	CO ₂	N_2	O ₂	H ₂ O
Biogas	0.597	0.4006	0.002	0.0004	0
Water	0	0	0	0	1

The first step was to select the thermodynamic method using the Aspen Method Assistant and Predictive Soave-Redlich-Kwong (PSRK) was the one recommended. Next, the chemical species involved in the simulation were introduced: methane, carbon dioxide, carbon monoxide, nitrogen, oxygen, water and hydrogen.

The raw materials considered are the ones mentioned before (biogas and water). Biogas importance had been expressed in the introduction and the water stream was required for the WGS reaction (2).

The schematic installation was represented in Fig. 2 and was the base for every scenario studied for the Aspen modelling represented in Fig. 3. This installation was divided in five sections:



Fig. 2. Schematic representation of the installation considered for Aspen simulation.



Fig. 3. Aspen Plus modelled process divided in five sections.

- Biogas intercooled compression
- Water compression
- Hydrogen production
- Product separation
- High Pressure Steam (HPS) production

1) Biogas intercooled compression

Biogas stream was compressed to a pressure of 16 bar, thorough an intercooled compression train, which consisted of 4 compressors with intermediate cooling.

Compression ratio was established at 4 and an isentropic efficiency of 0.75 [19]. All equipment names and details are mentioned in Table 2.

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1 able 2.	Diogas	COMDICISSION	specifications

Tuble 2. Diogus compression specifications				
Unit	Aspen model	Description	Operating conditions	
			Discharge	
C1	Compressor/	Compressor	pressure: 4 bar	
CI	Turbine	Compressor	Isentropic	
			efficiency: 0.75	
			Discharge	
C^{2}	Compressor/	Compressor	pressure: 8 bar	
C2	Turbine	Compressor	Isentropic	
			efficiency: 0.75	
			Discharge	
C2	Compressor/ Turbine	Compressor	pressure: 12 bar	
C5		Compressor	Isentropic	
			efficiency: 0.75	
			Discharge	
C4	Compressor/	Compressor	pressure: 16 bar	
C4	Turbine	Compressor	Isentropic	
			efficiency: 0.75	
INTC1	HootV	Heat	Hot stream outlet	
INICI	HeatA	exchanger	temperature: 80 °C	
INTCO	HootV	Heat	Hot stream outlet	
INTC2	HeatA	exchanger	temperature: 80 °C	
INITC2	HeatV	Heat	Hot stream outlet	
INTC3	пеатх	exchanger	temperature: 80 °C	

2) Water compression

The other reactant is water, which was compressed to 16 bar with no intermediate cooling, as the temperature rise is minimal between pumps. A compression ratio of 4 and an isentropic efficiency of 0.75 were considered, as well as the compression of biogas. Then, it was vaporized with a heat exchanger using flue gas from INT2. This has been compiled in Table 3.

1) Hydrogen production

Biogas and water were mixed after the compression and then pre-heated to an operating temperature between 700 °C and 900 °C depending on the scenario analysed. The different scenarios analyzed were:

- Scenario 1: Ceramic monolith, 700 °C.
- Scenario 2: Ceramic monolith, 800 °C
- Scenario 3: Ceramic monolith, 900 °C
- Scenario 4: Metallic monolith, 700 °C

- Scenario 5: Metallic monolith, 800 °C
- Scenario 6: Metallic monolith, 900 °C

Table 3. Water compression equipment and specifications				
Unit	Aspen model	Description	Operating conditions	
B4	HeatX	Heat exchanger	Cold stream outlet vapor fraction: 1	
P1	Pump	Pump	Discharge pressure: 4 bar. Isentropic efficiency: 0.75	
P2	Pump	Pump	Discharge pressure: 8 bar. Isentropic efficiency: 0.75	
Р3	Pump	Pump	Discharge pressure: 12 bar. Isentropic efficiency: 0.75	
P4	Pump	Pump	Discharge pressure: 16 bar. Isentropic efficiency: 0.75	

This operating temperature was suggested due to the highly endothermic reaction performed.

The pre-heat was performed with flue gas coming from the gas burner. In turn, this stream was pre-heated between the WGS reactors. Then, the biogas-water stream was heated a second time with the gas stream from the burner. Once the stream had the desired temperature, it was fed into the DRM reactor.

For the DRM reactor, a RPlug unity was considered, as it considers the reaction kinetic specifications, operating conditions and design data. DRM reactor's dimensions and specifications were height 30mm, diameter 16mm, catalyst mass 0.14 g [18] and a porosity of 0.42 for the metallic microreactor [18] and 0.6 for the ceramic monolith [20].

Next step was to introduce the kinetic data, with a Langmuir-Hinshelwood-Hougen-Watson (LHHW) reaction model. This kinetic type includes heterogeneous catalysis and considers three factors: kinetic factor, driving force and adsorption.

It is important to mention that two different reactions were considered: DRM reaction (1) and a secondary reaction (3) in which carbon monoxide and water are produced from carbon dioxide and hydrogen.

$$CO_2(g) + H_2(g) \to CO(g) + H_2O(g)$$
 (3)

The kinetic data was introduced in a simplified version, expressed in Eq. (4) and taking as the kinetic factor the unit value. Main reaction's kinetic data was obtained from J F Múnera *et al.*, 2007 paper [21], meanwhile secondary reaction's one was obtained from D. Triana Beltran's work [22].

One the DRM reaction finished, the product obtained was cooled to 457 °C with the tail gas from the PSA unit. The cooled stream is introduced into the high temperature steam reformer. In this reformer reaction described in Eq. (2) (WGS reaction) is driven.

The product stream obtained is cooled again with the condensed water coming from the condenser until the product temperature reaches 238 °C. This is the operating temperature of the low temperature steam reformer to produce the same reaction described in the previous paragraph.

Each unit specification has been expressed in Table 4, excluding the DRM reactor.

Table 4. Hydrogen production equipment specifications in exception of the DRM reactor

Unit	Aspen model	Description	Operating conditions
HTS- WGS	RStoic	High Temperature Steam Reformer	Temperature: 457 °C Pressure: 15,75 bar Equation 2 CO conversion: 0.75
INT2	HeatX	Heat exchanger	Cold stream outlet temperature: [700 – 900 °C]
INT3	HeatX	Heat exchanger	Hot stream outlet temperature: 350 °C
INT4	HeatX	Heat exchanger	Hot stream outlet temperature: 210 °C
LTS- WGS	RStoic	Low Temperature Steam Reformer	Temperature: 238 °C Pressure: 15.7 bar Equation 2
MIX1	Mixer	Mixer	-

2) Product separation

The produced hydrogen was separated from the rest of the components. First, the stream from LTS-WGS was expanded and then condensed at 38 °C to separate the unreacted water. This condensation was performed using as a cooling agent water intended for HPS production. Then, the dry stream was driven into a Pressure Swing Adsorption (PSA) unit, to finally separate hydrogen. Every equipment specification has been described in Table 5.

Table 5. Product separation equipment and specifications				
Unit	Aspen model	Description	Operating conditions	
B1	Compressor/ Turbine	Turbine	Discharge pressure: 4.8 bar	
CONDENSE	Flash2	Flash unit	Temperature: 38 °C Pressure: 1 bar	
INT5	HeatX	Heat exchanger	Hot stream outlet temperature: 38 °C	
PSA	Component Separator	Pressure Swing Adsorption	H ₂ split fraction: 1	

3) HPS production

The tail gas obtained from PSA unit had a strong methane concentration, so it was used for HPS production. This gas was mixed with air and the pre-heated with the outlet steam from HTS-WGS. Then, it was burned and, the resulting stream heated the reactant stream for DRM reactor and then used to produce HPS. Units' requirements were described in Table 6.

Table 6. HPS production specifications				
Unit	Aspen model	Description	Operating conditions	
COMBUST	RStoic	Gas burner	Temperature: 1654.6 °C	
INT6	HeatX	Heat Exchanger	Cold stream outlet vapor fraction: 1 Cold stream outlet pressure: 36 bar	
MIXER1	Mixer	Mixer	-	

B. Model Validation

Model validation was performed to verify the Aspen model. This ensures that the model reproduces, as far as possible, the monoliths activity and real behaviour. For this aim, experimental [17, 18] and Aspen data were compared through conversions and selectivity of the DRM reactor, represented in the following equations:

$$X_{CO2} = \frac{CO_{2,IN} - CO_{2,OUT}}{CO_{2,IN}} * 100$$
(4)

$$X_{CH4} = \frac{CH_{4,IN} - CH_{4,OUT}}{CH_{4,IN}} * 100$$
(5)

$$S_{H2} = \frac{H_{2,OUT}}{2(CH_{4,IN} - CH_{4,OUT})}$$
(6)

Being the subindex IN the molar flow of the chemical specie introduced in the reactor and OUT the outlet molar flow.

III. RESULT AND DISCUSSION

A. Simulation Model

The scenarios analysed were two different types of microreactors with an operation temperature between 700 and 900 °C. In every case a Rh/Al_2O_3 catalyst was supposed, as it is the one considered in the main references used for this work [17, 18]. Hydrogen and HPS production were represented in Tables 7 and 8.

Table 7. Hydrogen production depending on the scenario analysed. (Results expressed in kmol/h)

Temperature/ Microreactor	700 °C	800 °C	900 °C
Metallic	0.0517	0.0808	0.1139
Ceramic	0.0517	0.0808	0.1139

Table 8. HPS production on the scenario analysed. (Results expressed in kmol/h)

		/	
Temperature/	700 °C	800 °C	900 °C
Microreactor	700 C	000 C	900 C
Metallic	7.482	7.403	7.323
Ceramic	7.482	7.403	7.323

Then, a sensitivity analysis was performed, in which conversions, hydrogen and HPS production were compared only considering a ceramic microreactors in Figs 4 and 5. This is due to the results obtained in Tables 7 and 8, that shows that these productions do not change due to the material considered.

B. Model Validation

Once the mass and energy balances were made, a model validation was performed with experimental data obtained from bibliography and expressed in Table 9.

Table 9. Method validation according to the experimental studies [17, 18]

Reference	X _{CH4}	X _{CO2}	S _{H2}
Córdoba Rodríguez <i>et al.</i> , 2022 [17] (Ceramic microreactor, 700 °C)	3.4%	10.06%	77.45%
Navarro Puyuelo <i>et al.</i> , 2019 [18] (Metallic microreactor, 700 °C)	46.75%	30.03%	17.92%
Aspen simulation (Ceramic microreactor, 700 °C)	7.76%	11.59%	95.77%

It was only compared with the ceramic microreactor as conversion and selectivity did not change with the material type. The temperature in both experimental models was 700 °C. As represented, the results obtained were similar to the ceramic monolith case.

IV. CONCLUSION

This paper approaches modelling and validation of the DR

of methane, looking for the utilization and conversion of GHGs gasses. The Aspen simulation has been validated with experimental data from different references [17, 18], and it has shown that the model conversion of the reactants is close to the behaviour of a ceramic microreactor.

Considering the different scenarios proposed, it has been suggested that the material of the microreactor is not relevant to the conversion, but the operational temperature and catalyst mass have been. This is consistent with the nature of the reaction, as it is a very endothermic one. A major temperature shows a greater production of hydrogen but lower production of HPS due to the quantity of methane is destined to the gas burner and, therefore, heat to the HPS production.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

María Córdoba carried out the design and simulation of the DRM plant, Esmeralda Portillo and Benito Navarrete supervised and directed the main investigation, amending the errors in both calculations and in the text.

All authors had approved the final version.

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