Design and modeling of an autothermal co-flow reactor for turquoise hydrogen production

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Abstract
Within the current framework of the industrial processes it is noticeable a shift towards alternative and more green sources of energy: great attention has been focused on hydrogen utilization as energy carrier due to the major advantages brought by its combustion, thus receiving the attention of policy makers. Warming impact of continuous fossil fuels utilization could be mitigated introducing in the current energy mix environmentally friendly sources. Henceforth the motivation of this work, in which it is looked at a possible design for producing the so-called "turquoise hydrogen". The advantage of this design lies in the way heat is provided to the system – paired with the simple geometry of the reactor system. Analysis of performances, costs and environmental impact is provided in detail as well to highlight the large flexibility of the proposed design (according to different optimization criteria).

Introduction
Taking advantage of the large natural gas (NG) availability, one possible solution to produce clean hydrogen is represented by methane pyrolysis, giving rise to the "turquoise" hydrogen: thermal conversion of natural gas (96% methane content) in O_2-free environment, may aid the synthesis of such with the only by-product being solid carbon. Thus, giving the possibility of including a climate-friendly process chain that does not require any further downstream processing addressing CO_2 [1-3]. Relative to the solid carbon formation, different forms may be produced, each one of them having in common the same precursor being soot. Previous studies have helped in understanding how soot forms in relation to processing conditions [4]; yet some questions remain. Generally soot is said to be formed because of polycyclic aromatic hydrocarbons (PAHs) presence, and proper insights can be given if it is considered to combine a detailed gas-phase kinetic model, fluid dynamics and transport processes to the model for soot formation. Thus, in this work, a CFD model has been developed to quantify both the hydrogen and solid carbon production through a methane pyrolysis process. Such model has been adapted to design a simple reactor configuration, for understanding whether it is possible to achieve competitiveness with respect to the currently available technologies used for hydrogen production, being the aim of this study.

Methodology

In order to simulate the methane pyrolysis, the gas-phase reaction mechanism introduced is based upon a combustion model known as GRI-Mech [5]. The actual model used is truncated of the oxidation part to set up a model made of 104 reactions and 22 species – yet capable of closely reproducing combustion characteristics – named DRM 22. Deviation from the former mechanism is in the order of 2-4% [6].

For investigation of soot particle formation, it is introduced a computational model where a two-step procedure is followed according to Leung & Lindstedt [7]: a first phase of incipient particle formation is followed by surface growth through acetylene addition. Predicting its formation is deemed fundamental since good predictive model helps in regulating the formation of such as well as its removal. In the framework of the reactor in exam, within the simulation environment it was used a model named Moss-Brookes [8]. The soot fields described by that same model are soot particle number (*N*) and soot mass concentration (*M*) seen in *eq. 2-3*:

$$\frac{dN}{dt} = aN_A \left(X_{C_2H_2} \frac{P}{RT}\right)^l e^{-\frac{21100}{T}} - \left(\frac{24RT}{\rho_{soot} N_A}\right)^{\frac{1}{2}} d_p^{\frac{1}{2}} N^2 \quad (2)$$

$$\frac{dM}{dt} = aM_p \left(X_{C_2H_2} \frac{P}{RT}\right)^l e^{-\frac{21100}{T}} + b\left(X_{C_2H_2} \frac{P}{RT}\right)^m e^{-\frac{12100}{T}} \left[(\pi N)^{\frac{1}{3}} \left(\frac{6M}{\rho_{soot}}\right)^{\frac{2}{3}}\right]^n \quad (3)$$

a, l, b, m and n are model constant; P is the total pressure, N_A is the Avogadro number, d_p is the particle diameter, and X_i represents a mole fraction. Radiative interaction of soot is then addressed introducing the Weighted-Sum-of-Grey-Gases (WSGG) model, for definition of absorption coefficient.

In order to validate the model, results from the experimental investigation of Deutshcmann *et al.* [9] have been considered. Simulations are performed to match the experimentally recorded temperature profile as shown in *fig. 1* (for more detail please refer to [9]).

Table 1. Comparison between experimental and simulation data recorded at the tail end of the reactor (exp and sim respectively). Data source: [10]

T (K)	H_2 exp	H_2 sim	CH_4 exp	CH_4 sim	C_2H_2 exp	C_2H_2 sim
1473	0,862	0,765	0,111	0,171	0	0,051
1673	0,945	0,846	0,035	0,0458	0	0,103
1873	0,906	0,869	0,068	0,085	0	0,12

It can be noted that the accuracy of the prediction can be improved moving towards larger values of the temperature, maintaining the error within the 10% margin in the case of 1473K. Reasons of discrepancies in the carbonaceous compounds prediction are comprehensively explained in [10].

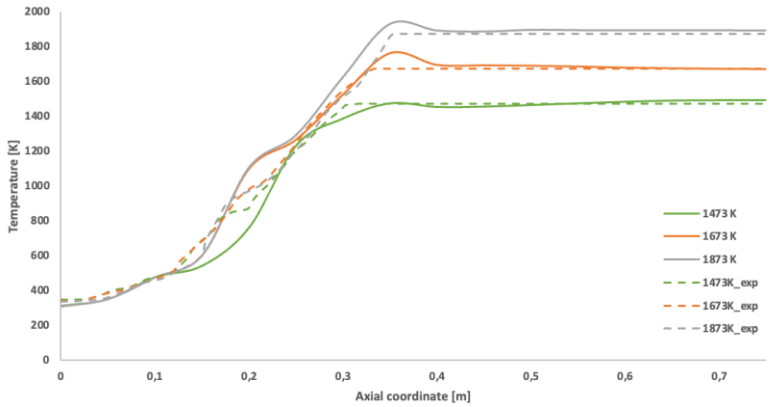

Figure 1. Numerically predicted temperature profile according to the chosen setup parameters.

Reactor design

Simulations have been performed adopting a design where a pyrolysis tube is enveloped in between exhausts of a methane/air stoichiometric flame produced upstream to the reactor itself (determining the possibility of having the so-called autothermal reactor): hence the presence of three streams – "M1" made solely of methane that undergoes pyrolysis, "FG1" and "FG2" which are composed of typical gaseous components of a flame with equivalence ratio 1.01 – arranged according to the scheme shown in *fig. 2*.
M1 is fed at ambient condition pressure and pre-heated to a temperature of 1000K, in a reactor which is made of three co-axial tubes having diameter of *2.6*, *5.0* and *8.0 cm* respectively, and a length of *60 cm* – co-axial laminar flows establishes in the latter. Streams have been introduced to have M1 in the middle tube and FG1-2 in the outwards ones. Setup parameter of interest is the flow rate with which FG1-2 are introduced – varying their velocity – allowing to regulate the temperature field developed in the tube.

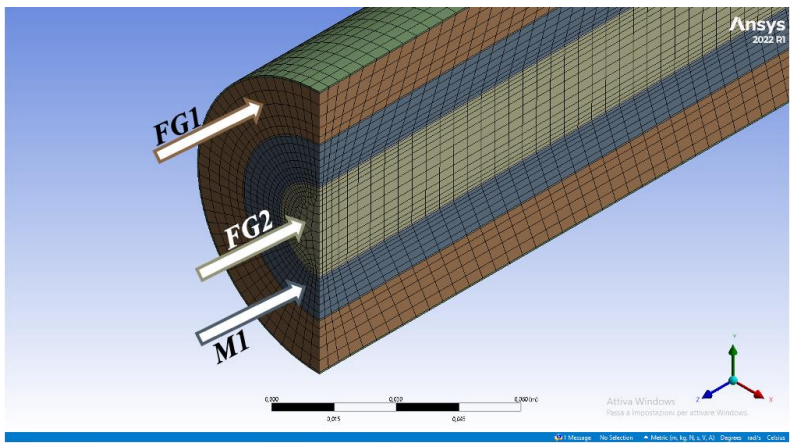

Figure 2. Streams arrangement on a half-section view of the reactor design in exam.

Results

Results from numerical predictions are obtained adopting the model and geometry reported in the previous section. The interest of this work lies in the performance parameters as well as the environmental and economic ones.

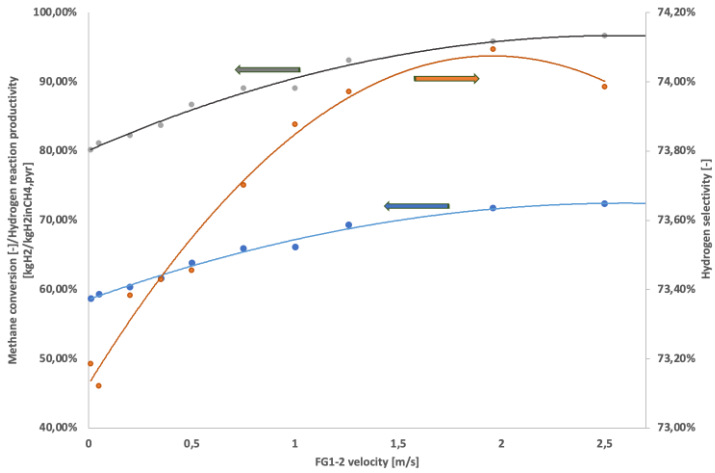

Figure 3. Methane conversion, H_2 reaction productivity and selectivity for different premix velocity cases (grey line is methane conversion, orange line is hydrogen selectivity, and blue line is hydrogen reaction productivity).

Reducing FG1-2 velocity, hydrogen purity is expected to be reduced because of the carbon residues and similarly does methane conversion: for sake of being coherent with the proposed idea, methane is intended to be exploited at best to avoid excess waste. Looking at hydrogen selectivity, it is looked to maintain the largest possible values because of the various carbonaceous gaseous products; the same goes for productivity.

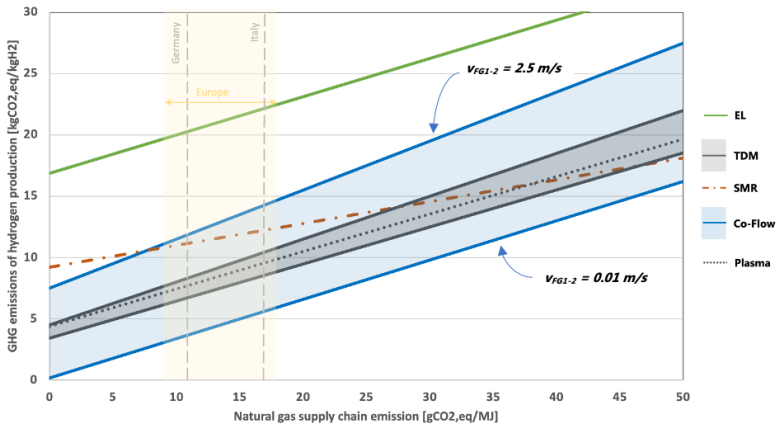

Figure 4. H_2 production GWI according to the natural gas supply chain GWI. Data for

methane pyrolysis are theoretical. Data source: Timmerberg *et al.* (2020) [11].

Moving to the Global Warming Impact (GWI, CO_2 emitted per unit of hydrogen produced) (*fig. 4*), it is noticeable the least amount of carbon emissions for low velocity systems – reasoning to be made is that approximatively it will be used a reduced amount of the required methane, thus producing less emissions. Reducing velocity to 1.96 m/s for FG1-2 already show to have fulfilled the desired task of having GWI smaller than that of steam methane reforming (SMR), representing the benchmark process to compare with (SMR is currently the most used technology for satisfying the hydrogen global demand [12]).

Finally, it can also be reported an economic analysis based on data reported in literature through the work of *Keipi et al.* (2018) [13].

Table 2. Comparison of main voices of costs between major hydrogen manufacturing technologies and the analyzed cases, expressed in k€/year for **OPEX** and k€ for *CAPEX* (Equipment cost is assessed via Peter, Timmerhaus & West (2003) [14]).

Technology /Cases	**CH_4 supply chain**	**CO_2 emission allowances**	**Electricity**	**O&M**	*Equipment*
TDM-SS	780	8	-	27	3233
TDMG-SS	547	42	6	24	2361
SMR-SS	618	61	11	87	10705
2.5 m/s	1135	33.7	-	111.8	5589
1.96 m/s	1064	26.65	-	104.8	5239.4
1.26 m/s	991	17.72	-	97.6	4880.6
1 m/s	996	14.74	-	98	4903.6
0.5 m/s	946.57	7.63	-	93.2	4661.02
0.05 m/s	936.10	0.82	-	92.2	4609.5
0.01 m/s	956.21	1.66	-	94.17	4708.47

Conclusion

Through the set of numerical data obtained it is possible to enable a comparison with respect to other hydrogen technologies, highlighting the real strength of such innovative design. At first, if it is looked at how those compare on an economic scale: the co-flow design looks to have the upper hand if it is possible to still have economically sustainable values of NG supply chain costs – second largest voice of cost to address (it is implicitly said that going on way large NG cost makes all the related technology not feasible on any scale).

Then, looking to the environmental scale, competitiveness with SMR can be achieved under current European NG supply chain condition: there will be region where it can be produced similar or even lower emission values – in favour of the autothermal technology.

It is important to clarify that ahead of the numerical solutions here presented, a more detailed analysis must be introduced. The information retrieved from the different simulations may serve as a tool for having a first optimization of the design to be built.

This analysis also highlights the main upside of the co-flow design, being its simple approach to the pyrolysis mechanism: it does not require downstream processing other than that related to heterogenous phases separation and does not ask for upstream treatment of natural gas. Finally, it can be concluded that overall, the selected design has behaved well in a wide range of operating conditions involving different temperature and species residence times.

Reference

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