Analysis of biphasic cracking of methane for hydrogen production using solar energy

Yazar(lar) (Author(s)): Rabah GOMRI¹, Belkacem NEZZARI²

ORCID¹: 0000-0002-8784-4614
ORCID²: 0000-0003-3202-0439


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Analysis of Biphasic Cracking of Methane for Hydrogen Production Using Solar Energy

** Araştırma Makalesi / Research Article**

**Rahab GOMRI**¹, Belkacem NEZZARI²

¹, ²University Mentouri Constantine 1, Department of Genie Climatique, 25000, Constantine, Algeria

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**ABSTRACT**

Hydrogen can be produced by many processes, by a series of chemical reactions many of which have been known for centuries. However, most of these reactions raise severe environmental and safety problems, while availability of raw materials is a critical problem. One of the partial solutions is solar hydrogen. It appears that cracking of carbon-rich materials is the right solution for this energy. In this context comes this numerical simulation of the methane cracking phenomenon. In the simulation, we have taken in to account the existence of carbon as a homogeneous powder. The mixture is considered to be biphasic formed by a gaseous phase with methane, hydrogen gases and carbon black powder solid phase. This powder is formed by solid particles with same diameter (d=50nm). The cracking phenomenon of the methane into hydrogen and carbon black takes place in a cylindrical cavity of 16 cm in diameter and 40 cm in length under the heat of concentrated solar radiation without any catalyst. A commercial calculation code "ANSYS FLUENT" is used to simulate the cracking phenomena. Two cases were studied: the first one applying a maximum solar radiation of 16MW/m² on the side wall of the reactor and the second one a maximum solar radiation of 5 MW/m². The CH₄ flow rate used at the inlet of the reactor is 0.4 L/min and the low Reynolds K-ε turbulence model was applied. A time step of 0.04s has been used. The cracking rate exceeds 90% with a maximum solar radiation of 16MW/m² and this rate does not reach 85% with a maximum solar radiation of 5MW/m². The dimensions of the cavity are important and it allows going from the experimental scale to the industrial scale. Working without any catalyst facilitates the separation of the elements after cracking.

**Keywords:** Hydrogen production, concentrated solar energy, methane, cracking.

1. INTRODUCTION

Solar energy is an abundant source of energy that can be utilized in two ways: (i) to convert sunlight into electricity through a photovoltaic system and (ii) to generate heat using concentrating collectors. Today, among the problems are climate change and ecological degradation, which are direct consequences of greenhouse gas emissions. Although any flammable material can theoretically be used as fuel, only a few are practically realistic. Some of them have low energy content and / or produce toxic gases and other polluting vapors during combustion, such as the pyrophoretic burning of iron particles [1]. The solution consists in the gradual introduction of clean energies. These energies are diverse and hydrogen is considered as one of these solutions, knowing that the combustion of hydrogen with pure oxygen results only in heat and water. Hydrogen can be produced by many processes, by a series of chemical reactions many of which have been known for centuries. However, most of these reactions raise severe environmental and safety problems; besides, the availability of raw materials is a critical problem. One of the partial solutions is solar hydrogen. According to Experimental works in the field of solar hydrogen production, it now appears that cracking of carbon-rich materials is the right solution for this energy for the following reasons:

- Thermolysis (dissociation of water) can be considered as a perfect process but it requires special equipment to withstand the high temperatures required and to separate the two gases produced (O₂, H₂) which form a highly explosive mixture [1-5] and its cost compared to the output is still a major problem.
- Thermo-chemical cycles [2, 5-13] with two steps taking place under moderate temperatures, require the preparation of the metal oxides or others used in chemical reactions. These cycles also require special equipment and major problems of contamination are posed. Gasification or reforming of carbon-rich materials also generates greenhouse gases such as CO₂ and toxic gases such as CO [1, 5, 15].

The cracking of carbon-rich materials such as methane [1-3, 16-18] allows us to produce hydrogen without releasing greenhouse gases and without toxic components. Improved combustion by minimizing emissions of environmentally hazardous gases by injecting hydrogen into Gas networks and the availability of methane in the world are sufficient criteria to propose this study of the

- simulation of the cracking of methane in a tubular reactor under concentrated solar heat.
Biomass-to-hydrogen processes, including gasification, pyrolysis, and fermentation, are less well-developed technologies. These processes offer the possibility of producing hydrogen from energy crops and from biomass materials such as forest residue and municipal sewage. Solar energy can be used to produce hydrogen from water and biomass by several conversion pathways. Concentrated solar energy can generate high temperatures at which thermochemical reactions can be used to split water. Photoelectrochemical water splitting and photobiology are long-term options for producing hydrogen from water using solar energy. All these technologies are in the development stage[1,19].

2. THERMODYNAMIC AND THEORY

Kinetic scheme:
We consider that the cracking is governed only by the chemical reaction given by Equation (1):

$$\text{CH}_4 \rightarrow C(s) + 2\text{H}_2 \quad (1)$$

The constant rate in the forward direction of the reaction is calculated using the Arrhenius expression

$$k_{f,r} = A_r T^\beta_r e^{-E_r/RT} \quad (2)$$

Where

- $A_r$: Pre-exponential factor ($s^{-1}$)
- $T$: temperature (K)
- $\beta_r$: Temperature factor (-)
- $E_r$: Activation energy (J/kgmol)
- $R$: Universal gas constant (J/kgmol.K)

Carbon is considered as a solid powder. The constant rate of progress of the chemical reaction is calculated by applying the Arrhenius law. Assuming that reaction (1) is of order 1 ($\beta_r = 0$) and according to [16], the activation energy is equal to 147x10^6 J/mol and the pre-exponential factor is equal to 1x10^5 s^-1[16]. The flow is reactive and moreover it is inverted for geometrical reasons which allow us to consider it turbulent despite the low Reynolds number.

Parameters of simulation and flow rate choice:
The properties of materials used in this study are given in Table 1. We chose to work under high temperature and under atmospheric pressure because these conditions favor the cracking of methane [14].

3. CRACKING GEOMETRY AND BOUNDARY CONDITIONS

Reactor Geometry:
The geometry of the cavity in which cracking takes place and the chosen boundaries conditions are shown in Figure 1. The mesh is made by mesh software “Gambit”. The wall effect is taken into consideration. The reactor chosen in this simulation is a cylindrical cavity in which is placed a core containing a tubular void allowing injection of the methane.

![Figure 1. Form of the reactor assumed to be filled by the polyphase mixture](image)

The side opposite to the inlet of the methane is subjected to solar radiation whereas Figure 2 shows only the volume of the gas mixture resulting from the chemical reaction of the cracking taking place in the reactor under the effect of the solar heat. The problem is considered two-dimensional. For reasons of symmetry with respect to the axis of the cavity, the meshed surface represents half of a longitudinal section taken along the reactor (in dashed lines).
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Calculation domain and boundary conditions:
Figure 3 shows geometry of the calculation domain and boundary conditions.

Where:
1- orifice (methane inlet): orifice of methane injection when \( Q = 0.4 \) L/min
2- Wall subjected to solar radiation: it is assumed that there are 3 zones, the first zone is a circle of 6 mm in diameter subjected to flux radiation \( q_1 \), the second is annular of 3 mm of inner radius and 20 mm of outer radius, subjected to flux radiation \( q_2 \) while the third is also annular with 20 mm inner radius and 80 mm outer radius, subjected to flux radiation \( q_3 \).
3- Outer longitudinal walls (adiabatic): the reactor is in a very hot atmosphere, so we neglect any heat exchange between the external walls of the reactor and this atmosphere \( \left( \frac{\partial T}{\partial y} \right)_{y=80 \text{ mm}} = 0 \).
4- Inner longitudinal walls (adiabatic): these walls represent the limits of the reactor core so they are considered adiabatic (no heat exchange in the radial direction from the axis of symmetry) \( \left( \frac{\partial T}{\partial y} \right)_{y=3 \text{ and } 20 \text{ mm}} = 0 \).
5- Reactor output: no conditions imposed on the reactor outlet.
6- Symmetry: The flow is supposed to be independent of the angle of rotation along the axis of symmetry; this allows us to reduce the mesh of 3 dimensions to a mesh of 2 dimensions according to a plan of longitudinal section which is symmetrical w.r.t. the axis of rotation of the reactor.
7- Lateral wall (adiabatic): these walls represent the limits of the reactor core so they are considered adiabatic (no heat exchange in the axial direction) \( \left( \frac{\partial T}{\partial x} \right)_{x=380 \text{ mm}} = 0 \).

Flow rate:
In this simulation, we operated with a flow rate used in the experimental work used by Flamant [14 - 15] when \( Q = 0.4 \) L/min and applying the low Reynolds K-\( \varepsilon \) turbulence model. A commercial calculation code "ANSYS FLUENT" is used to simulate the cracking phenomenon.
Firstly, 16MW/m² thermal solar radiation at the reactor focus is used assuming that the carbon powder is homogeneous with an average diameter of 50 nm for its particles. To choose an average diameter of 50 nm, we based on [14] when the carbon powder collected in the filter was amorphous and the diameter of particles was in the range 20–100 nm.

4. RESULTS AND DISCUSSION
As shown in Figure 4, at time \( t = 5 \) seconds most of the methane is converted to hydrogen. At this time, the quantity of methane injected is not important, for this
reason, the methane is almost completely converted to hydrogen.

Table 2 summarizes the hydrogen mass fractions obtained by simulation while applying a maximum radiation of 16 MW/m² to the side wall of the reactor, as shown in Figure 4, bearing in mind that we used [11-14] to choose values between 16 and 1 MW/m².

![Figure 4. H₂ Contour in the zone for cracking a biphasic mixture at t = 5 seconds](image1)

<table>
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<tr>
<th>t (s)</th>
<th>H₂ Fraction</th>
<th>t (s)</th>
<th>H₂ Fraction</th>
<th>t (s)</th>
<th>H₂ Fraction</th>
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</tr>
</tbody>
</table>

Figure 5 shows the mass fraction of carbon through the reactor at time t = 27s, knowing that ANSYS FLUENT calculates each phase separately. It is clear that at the reactor inlet, the fraction of the carbon is equal to zero and as at t=27s, the reactor becomes entirely hot, which allows the cracking of methane before reaching the wall subjected to concentrated solar radiation.

![Figure 5. Contours of mass fraction of carbon – solid at time 27s](image2)
Figure 6 summarizes the percentage of hydrogen obtained by simulation by applying a maximum radiation of 16 MW/m² on the side wall of the reactor as shown in Figure 4, based on work of [16-19] to select values between 16 and 1 MW/m². Initially (t = 0s) the reactor is empty, any quantity of the gas will be cracked but over time these quantities become important and they require more energy which influences the conversion of methane and cracking rate decreases but it resumes when the time goes by under the effect of the transport of energy by the flow (see Table 1). At 27 seconds, the permanent regime is reached. An average value of H₂ fraction of about 92% is obtained. By applying the same solar concentration and the same flow rate, Flamant [14-15] (page 85 Table 3) obtained a maximum cracking rate of 91.4%.

Figure 7 gives the profiles of the static temperature of the gas phase obtained by simulation between 1 and 27 seconds along the reactor.

Figure 8 summarizes the percentage of hydrogen obtained by simulation while applying a maximum radiation of 5 MW/m² on the side wall of the reactor as shown in Figure 4, based on work of [11-16] to select values between 5 and 1 MW/m² (q₁ = 5 MW/m², q₂ = 2 MW/m² and q₃ = 1 MW/m²). As the previous case and initially (t = 0s) the reactor is empty, the first quantities of methane will be cracked (between 0 and 5 seconds) and with time these quantities become important (between 10 and 40 seconds) and the conversion of these methane quantities, require more energy and therefore the cracking rate decreases but this cracking rate resumes and increases again from the 40th second under the effect of the transport of energy by the flow. At time about 90 seconds the permanent regime is reached. An average value of H₂ fraction of about 81% is obtained.

Figure 9 gives the profiles of the static temperature of the gas phase obtained by simulation between 5 and 90 seconds along the reactor.

Figure 10 shows the difference in temperature along the reactor for the mentioned cases. We chose to compare the temperature of the two cases at the same moments (5, 10, 20 and 27 seconds). It can be seen that the temperatures of the case where the maximum radiation is 16 MW/m² are greater than those in which the maximum solar radiation is 5 MW/m². Since the reaction is endothermic, it consumes the energy needed for cracking and the rest of the energy is used to heat the mixture after cracking and likewise this energy will be transported by the flow. This explains that the energy transported in the case of 16000 suns is greater compared to the case of 5000 suns and this explains the difference of the temperatures of the two cases and consequently we obtain the difference in the cracking rates as shown in the next figure (Figure 11).
Comparison of the fractional profiles of the hydrogen obtained by simulation at the reactor outlet

CONCLUSIONS
In this paper a detailed comparative study of two phase methane cracking using concentrated solar energy is carried out for flow rate of methane of 0.4L/min. The cracking rates of 91.4% (maximum solar radiation of 5MW/m²) are greater than those in which the maximum solar radiation is 16 MW/m². This rate does not reach 85% with a maximum solar radiation of 16MW/m² and this rate does not reach 85% with a maximum solar radiation of 5MW/m².

REFERENCES


