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

Araştırma Makalesi / Research Article

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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/m^2 on the side wall of the reactor and the second one a maximum solar radiation of 5 MW/m^2. The CH_4 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/m^2 and this rate does not reach 85% with a maximum solar radiation of 5MW/m^2.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 theproblems 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 (O_2, H_2) 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 CO_2 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.

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Table 1. Materials properties (all properties are given by ANSYS FLUENT database)

materials	Molecular weight (kg/kgmol)	Density (kg/m^3)	Specific heat (J/kg-k)	Thermal condutivity	Viscosity (kg/m.s)
Methane	16.04303	0.669	0.033	Piecewise polynomial	1.087e-05
Hydrogen gas (H_2)	2.01594	0.08189	polynomial	polynomial	polynomial
Carbone-solid	12.01115	2000	Piecewise	0.33	1.72e-05

- 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.THERMODYNAMY AND THEORY

Kinetic scheme:

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

$$CH_4 \rightarrow C(s) + 2H_2 \qquad (1)$$

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

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

Where

A_r : Pre- exponentiel factor (s^{-1})

T: temperature (K)

β_r :Temperature factor (-)

E_r : Activation energy (J/kgmol)

R : Universel gas constant (J/kgmol.K^4)

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 1x10^6 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 prpperties 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.

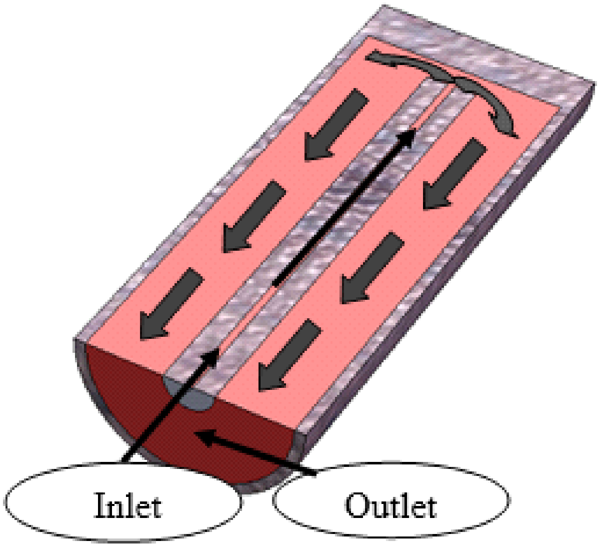

Figure 1. Form of the reactor assumed to be filled by the polyphase mixture

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).

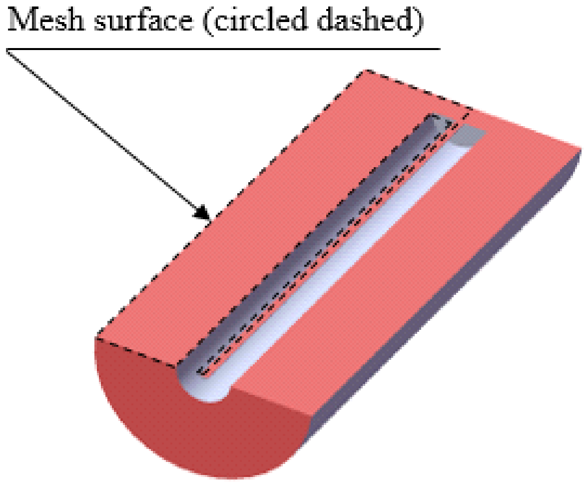

Figure 2. Internal volume of the reactor occupied by the half-section mixture

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) $(\frac{\partial T}{\partial y}\Big|_{y=3\ and\ 20\ mm}) = 0$

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 allowsus to reduce the mesh of 3 dimensions to a mesh of two dimensions according to a plan of longitudinal section which is symmetrical vis a vis 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 $(\frac{\partial T}{\partial x}\Big|_{x=380mm}) = 0$

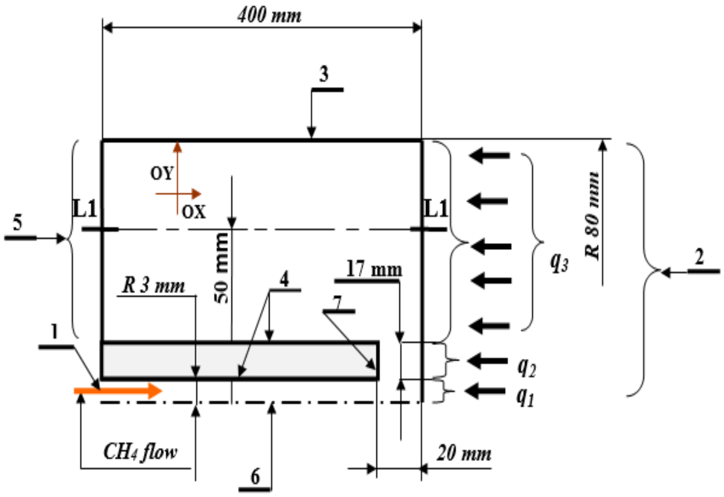

Figure 3. Geometry of the calculation domain

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 6mm in diameter is subjected toflux radiation q_1, the second is annular of 3mm of inner radius and 20mm of outer radius, is subjected to flux radiation q_2 while the third is also annular with 20mm inner radius and 80mm outer radius, is subject 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 $(\frac{\partial T}{\partial y}\Big|_{y=80mm}) = 0$.

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 - ε turbulence model. A commercial calculation code "ANSYS FLUENT" is used to simulate the cracking phenomenon.

Firstly, 16MW/m^2 thermal solar radiation at the reactor focus is used assuming that the carbon powder is homogeneous with an average diameter of 50nm for its particles. To choose an average diameter of 50nm, 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 =5seconds 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/m^2 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/m^2

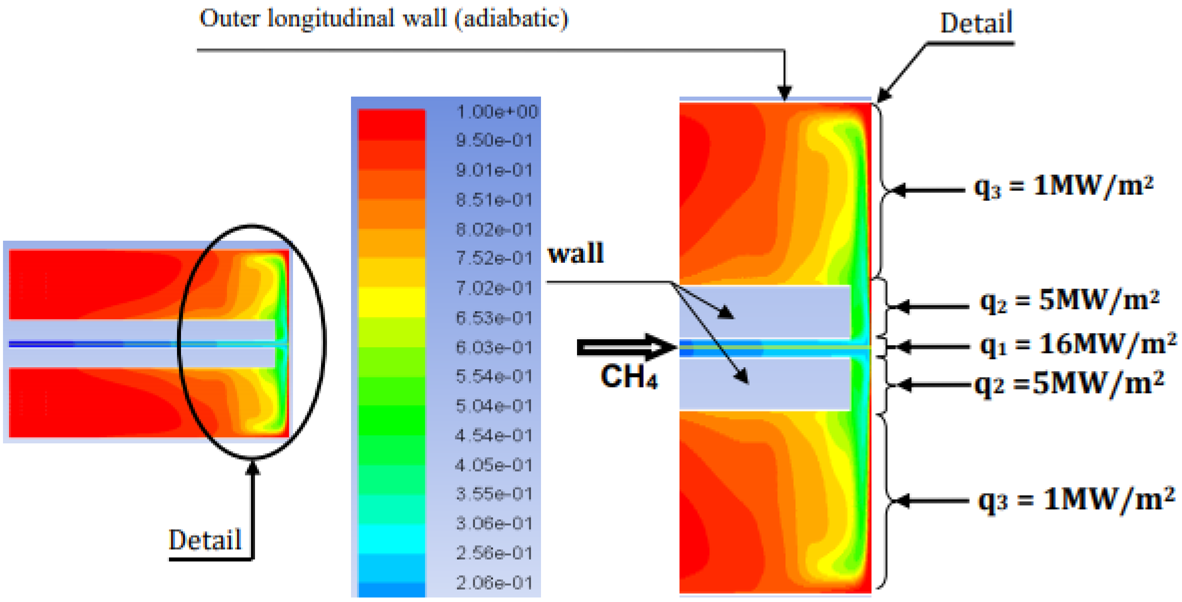

Figure 4. H_2 Contour in the zone for cracking a biphasic mixture at t = 5seconds

Table 2: Hydrogen mass fractions obtained at the reactor outlet

t (s)	H_2 Fraction	t (s)	H_2 Fraction	t (s)	H_2 Fraction
4	0.99358989	12	0.91048795	20	0.90799227
5	0.98986295	13	0.90584034	21	0.91100136
6	0.97666023	14	0.90250364	22	0.91407602
7	0.96304818	15	0.90082000	23	0.91651239
8	0.95060989	16	0.9003958	24	0.91877511
9	0.93956432	17	0.9011825	25	0.9214575
10	0.92897375	18	0.9029467	26	0.92427511
11	0.91810557	19	0.90528852	27	0.92692068

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.

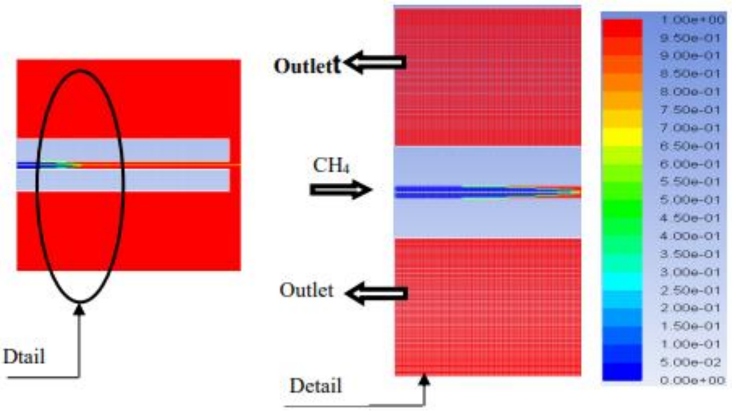

Figure 5. Contours of mass fraction of carbon – solid at time 27s

Figure 6 summarizes the percentage of hydrogen obtained by simulation by applying a maximum radiation of 16MW/m^2 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/m^2. 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 H_2 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%.

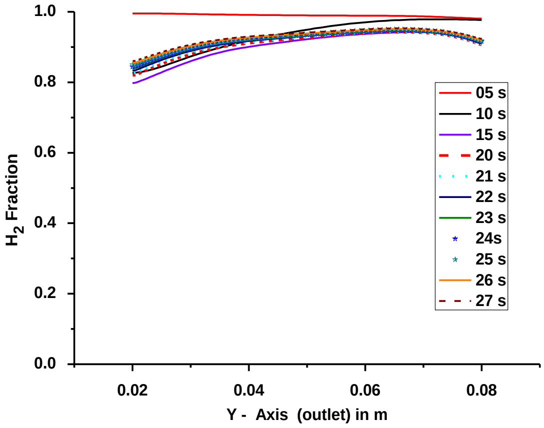

Figure 6. H_2 mass fraction profiles obtained by simulation between 5and 27 seconds with maximum solar radiation of 16MW/m^2

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

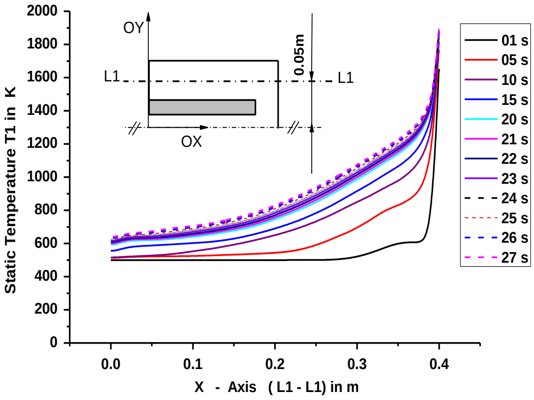

Figure 7. Profiles of the static temperature of the gas phase obtained by simulation between 1 and 27 second along the reactor with maximum solar radiation of 16MW/m^2

Figure 8 summarizes the percentage of hydrogen obtained by simulation while applying a maximum radiation of 5MW/m^2 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/m^2 (q_1=5MW/m^2, q_2=2MW/m^2 and q_3=1MW/m^2). As the previous case and initially (t = 0s) the reactor is empty, the first quantities of methane will be cracked (between 0 and 5seconds) and with time these quantities become important (between 10 and 40seconds) and the conversion of these methanequantities, 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. Anaverage value of H_2 fraction of about 81% is obtained.

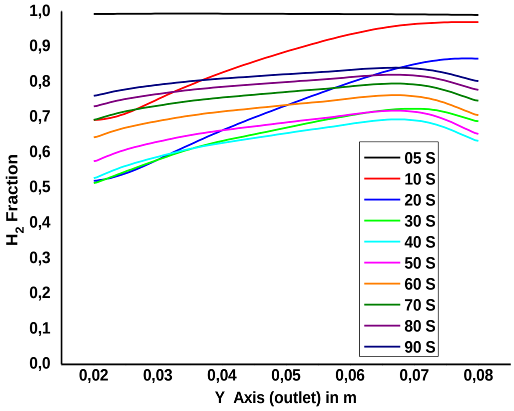

Figure 8. H_2 mass fractions profiles obtained by simulation between 5 and 90 seconds with maximum solar radiation of 5MW/m^2

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/m^2 are greater than those in which the maximum solar radiation is 5MW/m^2.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).

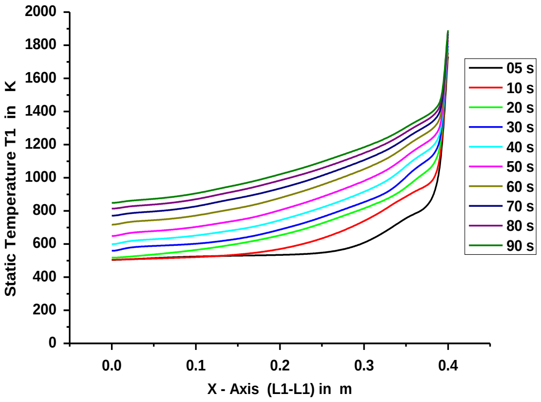

Figure 9. Profiles of the static temperature of the gas phase obtained by simulation between 5 and 90 seconds along the reactor (maximum solar radiation of 5MW/m^2)

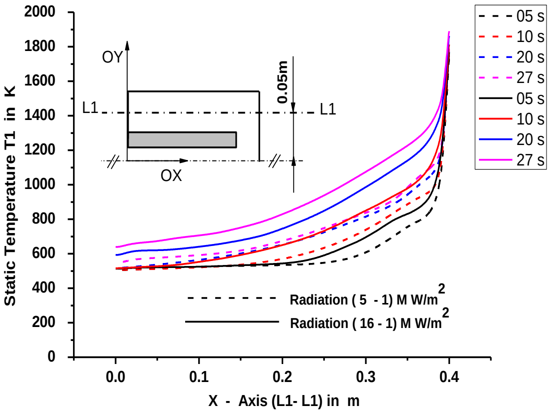

Figure 10. Comparison of the static temperature profiles obtained by simulation between 5 and 27 seconds along the reactor

In Figure 11, it is clear that the cracking rate depends on the solar radiation whatever the cracking time. It is shown that the cracking rate exceeds 90% with a maximum solar radiation of 16MW/m^2 after a time of 27 seconds and this rate does not reach 85% after a time of 90 seconds with a maximum solar radiation of 5MW/m^2.by applying the same solar concentration and the same flow rate, Flamant [14 -15(page 85 tabl 3] obtained a maximum cracking rate of 91.4%.

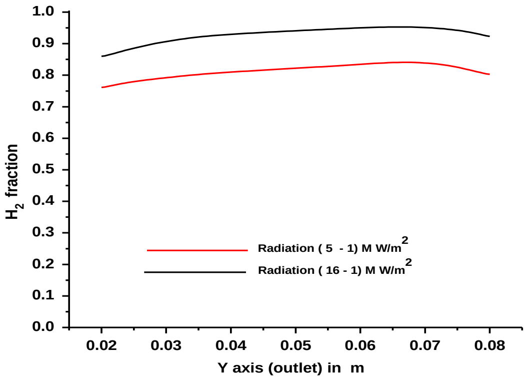

Figure 11. Comparison of the fractional profiles of the hydrogen obtained by simulation at the reactor outlet

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 temperatures of the case where the maximum radiation is 16 MW/m^2 are greater than those in which the maximum solar radiation is 5MW/m^2 and consequently the difference in the cracking rates is obtained. The cracking rate exceeds 92% with a maximum solar radiation of 16MW/m^2 and this rate does not reach 85% with a maximum solar radiation of 5MW/m^2.

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