Research note

Investigation of Sour Natural Gas Decomposition in a Nozzle-type Solar Reactor for Hydrogen Production

M. Javadi[*1], M. Moghiman[2], F. Faridnia[2]
1- Department of Mechanical Engineering, Quchan Institute of Engineering and Technology, Iran
2- Department of Mechanical Engineering, Ferdowsi University, Mashhad, Iran

Abstract
Eventual realization of a hydrogen economy requires cheap and readily available hydrogen sources and a technology to convert them into pure hydrogen in an efficient and sustainable manner. The objective of this paper is the computational investigation of the hydrogen production through thermal decomposition of sour natural gases containing CH_4 and H_2S inside a solar reactor. In this study a solar reactor has been used to absorb solar power and allow it to concentrate in a graphite nozzle in the middle of the reactor and transfer it to a flow reactant thereafter. From an economical standpoint, the main issue is the production of two valuable products, hydrogen (H_2) and a high-value nano-material of carbon. The effects of H_2S to CH_4 feed ratio and reactor temperature on hydrogen, carbon black, S_2 and CS_2 formation are investigated. The results show complex behavior in the products, because of the difference in CH_4 and H_2S pyrolysis temperatures. It can be seen that for $H_2S/CH_4>2$, the yields of H_2 and CS_2 reach a local and global maximum at $H_2S/CH_4=5$, respectively. A comparison performed between the presented results and the results of Towler and Lynn, and Abanades demonstrates a good agreement.

Keywords: *Hydrogen Sulfide, Pyrolysis, Solar Reactor, Hydrogen, Sulfur Compound*

1. Introduction
Scientists promote hydrogen as a potential fuel for motive power, the energy demands of buildings, and portable electronics. Hydrogen is well known as an ideal and clean source of energy which is believed to reduce the emission of carbon dioxide and therefore play a major role in decreasing global warming [1]. Using a combination of hydrogen and available renewable energy instead of petroleum fuels can be a good solution to the lack of energy sources.

Eventual realization of a hydrogen economy requires cheap and readily available hydrogen sources and a technology to convert them into pure hydrogen in an efficient and sustainable manner [2]. In addition to water, which is an ideal hydrogen source, CH_4 and H_2S are considered as alternative sources of hydrogen [2, 3]. On the other hand, there is ample scope for CH_4 and H_2S as the raw source of H_2, because the energy required for CH_4 and H_2S splitting ($\Delta H_{CH4}=74.9$ kJ/mol and $\Delta H_{H2S}=79.9$

∗ Corresponding author: mohammad.javadi@gmail.com

kJ/mol) is much less than water splitting (ΔH_{water}= 284.7 kJ/mol) [4]. There are several convenient technologies for production of H_2 from CH_4, including steam methane reforming (SMR), partial oxidation, pyrolysis, autothermal pyrolysis, and autothermal SMR [5]. Methane decomposition is a moderately endothermic reaction. It requires much less thermal energy (only 37.8 kJ per mol of hydrogen produced) than SMR (69 kJ/mol H_2). In addition to the decrease in the required energy, the CO_2 emission is also decreased in this method. Methane, as the main component of high quality natural gas can be decomposed to hydrogen and carbon black in the solar reactor [6]. As the main impact, H_2 is produced with renewable energy and is not contaminated by combustion by-products. Furthermore, solar energy is stored as a transportable fuel and no CO_2 emission occurs during the process [7,8]. Hydrogen sulfide (H_2S) is a common contaminant in many of the world's natural gas (NG) wells. Approximately one-third of US NG sources can be considered as low or sub-quality gas that is not suited for pipeline shipment [9]. H_2S concentration in NG varies from traces to 90% by volume. In natural gas processing, H_2S is known as a pollutant because it corrodes pipelines and deactivates metal-based catalysts used in steam methane reformation (SMR). Therefore, it is obviously of considerable concern in global source utilization and climate change implications. Gas flaring has also been blamed for environment and human health, causing problems such as acid rain, asthma, skin and breathing diseases [10].

As mentioned above, production of hydrogen from sub-quality natural gas (SQNG) is a feasible option which utilizes this untapped energy source and results in reducing the carbon oxide and hydrogen sulfide emissions. In a solar reactor, thermal decomposition of CH_4+H_2S produces hydrogen, carbon, and other sulfur compounds [6]. Therefore, the production of hydrogen by solar reactor has recieved great consideration recently. Petrasch et al have studied hydrogen production process using solar reactors with SMR method [11]. Abanades et al also investigated the effect of different parameters and system geometry on methane conversion and hydrogen yield using thermal decomposition method in solar reactors [6, 7]. The results show that the solar reactor producing pure H_2 has high efficiency in CH_4 conversion. In addition, Towler and Lynn introduced thermal decomposition of hydrogen sulfide at high temperature as an alternative of Clause process [12]. The main advantage of the thermal decomposition is reduction of produced tail gas rather than the Clause process. They have investigated the effect of the presence of CO_2 in feed gas and temperature on decomposition and sulfur compounds production. Based on the advantages of thermal decomposition methods in comparison with the steam methane reformation method, in this paper the hydrogen production process from sour natural gas has been studied using the proposed reactor by Abanades [6].

2. Chemical reaction modeling
The chemical reaction occurs in a reactor by receiving solar energy as the energy source. The basic geometry of the solar reactor is shown in Fig. 1, consisting of the pyrex glass

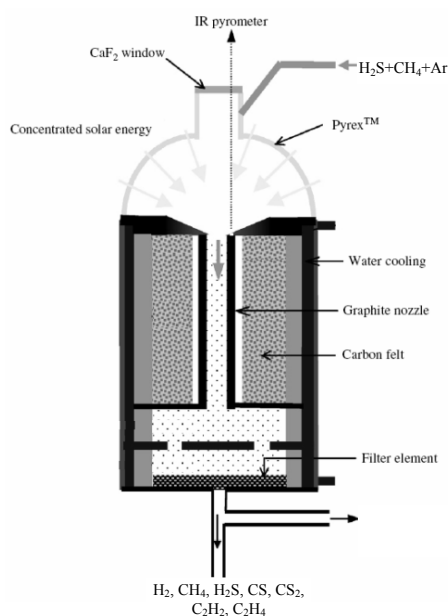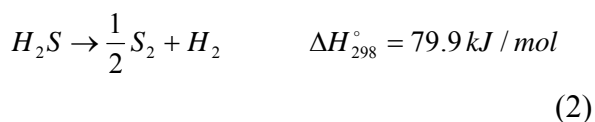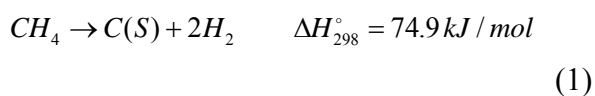window, the gas input, the graphite nozzle, and the gas outlet [6].

Figure 1. Solar reactor [6]

The gas flowing in the nozzle, positioned in the center of the reactor, is a mixture of Ar, CH_4, and H_2S. The power absorbed by solar energy is concentrated in the graphite nozzle. Production of hydrogen through thermolysis of SQNG involves a complex series of chemical reactions which control conversion of both CH_4 and H_2S as follows [3, 12]:

$$CH_4 \rightarrow C(S) + 2H_2 \qquad \Delta H^\circ_{298} = 74.9 \, kJ/mol$$
(1)

$$H_2S \rightarrow \frac{1}{2}S_2 + H_2 \qquad \Delta H^\circ_{298} = 79.9 \, kJ/mol$$
(2)

Reaction 1 requires temperatures higher than $850\,^\circ K$ to proceed at reasonable rates [13] and in reaction 2 temperatures above $1500\,^\circ K$ are required for achieving reasonable rates [9]. Thermodynamics of

thermal CH_4 decomposition calculate that reaction (1) is complete at about 1300K [7]. Under special circumstances like using a catalyst, H_2S can react with methane producing carbon disulfide (CS_2) and H_2 [3].

$$2H_2S + CH_4 \Leftrightarrow CS_2 + 4H_2 \qquad \Delta H^\circ_{298K} = 232 \, kJ/mol$$
(3)
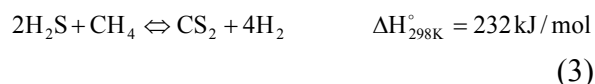
The kinetic mechanisms of thermal CH_4 decomposition are stepwise dehydrogenation at high temperature ($2CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow 2C$), which is included in the chemical reactions model of the reactor [7].

## 3. Turbulence–chemistry interaction

The Probability Density Function (PDF) method is used to model the turbulent chemical reactions occurring in the diffusion, combustion, and thermal decomposition of natural gas in the carbon black furnace. This method, which assumes the chemistry is fast enough for a chemical equilibrium to always exist always at molecular level, enables handling of large numbers of reacting species including intermediates. Transport equations are solved for the mean mixture fraction $\bar{f}$, its variance $\overline{f'^2}$, and enthalpy $\bar{h}$. Calculations and PDF integrations are performed using a preprocessing code, assuming chemical equilibrium between 30 different species. The particular mechanism used in this study is validated under the considered conditions by references [6, 9, and 12].

The results of the chemical equilibrium calculations are stored in look-up tables by use of pre-PDF preprocessor in Fluent software, which relate the mean

thermochemical variables (species mass fractions, temperature, and density) to the values of $\bar{f}$, $\overline{f'^2}$, and $\bar{h}$ [14].

4. Numerical solution procedure

The solar reactor used in this work is identical to that reported previously by Abanades [6]. The reactor has been simulated by a 2D axisymmetrical model using a CFD software, Fluent. Gambit preprocessor is used for a two dimensional geometry creation and unstructured grid generation. The 2D volume grid is represented in Fig. 2. In the present model, the carbon felt and water cooling system is ignored and absorbed solar energy is directly imposed to the inner walls of the nozzle. The domain is discretized into a grid of 9536 nodes and 9225 quadrilateral cells. The conservation equations for mass, momentum, energy, Reynolds stresses, dissipation rate, mixture fraction and its variance are solved using a second-order upwind scheme for discretization of the convective terms in the transport equations. The radiative heat transfer in the absorbing, emitting and scattering medium is calculated by the Discrete Ordinates (DO) radiation model [15]. The RNG k-ε model is used for turbulence modeling inside the reactor [16]. These models, used in fluid flow mechanics, heat transfer, mass transfers, and chemical reactions are allowed to interpret the experimental results [6, 12]. The numerical investigation aims at predicting fluid flow characteristics, temperature distribution, CH_4 and H_2 concentration profiles, and conversion rates as a function of process parameters.
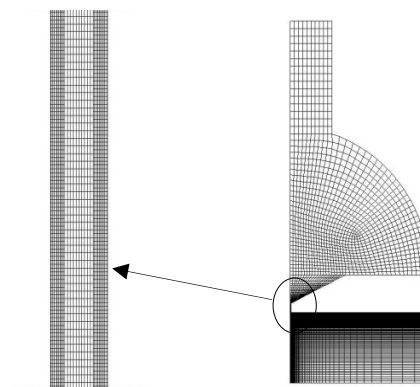
Figure 2. Two-dimensional quadrilateral grid of reactor model

5. Results

Numerical calculations have been performed on the gas flow inside the reactor described by Abanades [6] shown in Fig. 1. The total inlet flow rate of the reactor is 80 lit/hr, at 473 K. The absorbed solar energy increases the temperature of the nozzle so that a constant heat flux of 15000 W/m^2 is assumed to be imposed to the inner walls of the nozzle. The results with pure CH_4 and a mixture of CH_4 and H_2S feed gas are compared with the results of Abanades [6] and Tawler & Lynn [12], respectively. A comparison between the H_2S conversion and S_2 yield predicted by this model, and Towler & Lynn's results [12], is presented in Fig. 3 which shows a good agreement. The results discrepancy is caused mainly by chemical reactions modeling method and neglecting flow effects in the Towler model.

Another validation is performed on the molar concentration of H_2 in radial direction from the nozzle axis in Fig. 4. The molar concentration of H_2 increases from the center to the graphite nozzle, heated by concentrated solar energy.
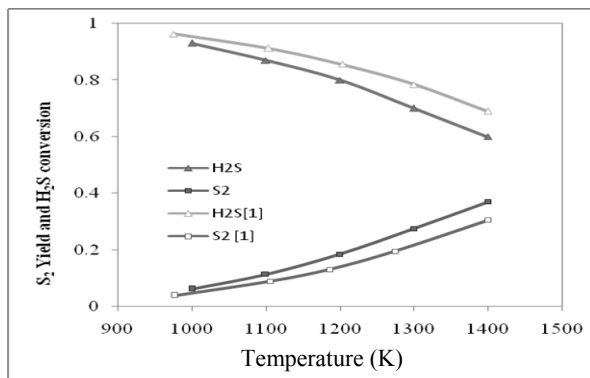
Figure 3. Comparison of the predicted of S_2 yield and H_2S conversion with the result of Towler and Lynn [12]
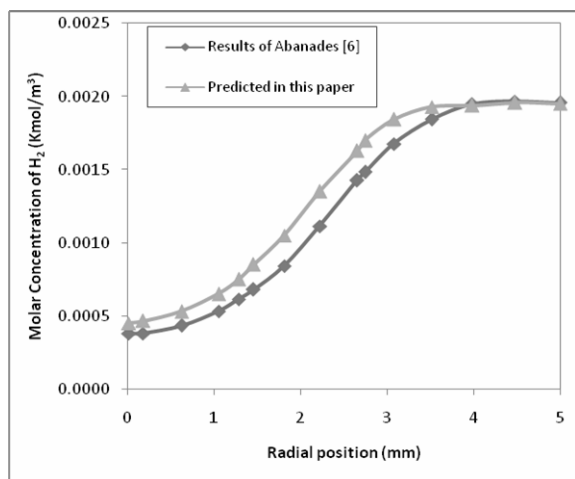

Figure 4. Comparison of molar concentration of H_2 with the result of Abanades [6]

The variations of H_2 yield with CH_4 conversion are also shown in Fig.5. Comparison of the presented results with the predicted results by Abanades[6] demonstrates good agreement. Validation of the chemical model included formation of H_2, C_2H_2, C_2H_4, and C_2H_6 from CH_4 decomposition. As a result of the significance of H_2 production, a comparison of the H_2 yield with Abanades results has been performed ignoring other produced, components.

At first, the formation process of different species inside the nozzle has been studied for

80 lit/hr flow rate at the inlet, 0.9 mass fraction of Argon in feed gas, and $H_2S/CH_4=1$. Then the effect of H_2S/CH_4 in the production of different species has been considered. The mass fraction of the produced species and temperature distribution in the nozzle are represented in Fig. 6. As shown, CH_4 decomposition reaction, unlike that of H_2S, begins close to the inlet of the nozzle. Fig. 7 shows the variations of CH_4, H_2S, and H_2 mass fraction versus axial position.
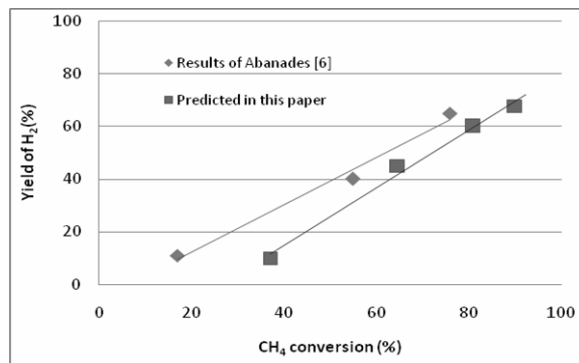

Figure 5. Comparison of predicted H_2 yield versus CH_4 conversion with the result of Abanades [6]

CH_4 mass fraction is maximum at the inlet of the nozzle. It decomposes rapidly passing through the nozzle so that CH_4 is converted completely at L=0.03. Since methane decomposition is a mildly endothermic reaction, the temperature of the mixture decreases. As a result, H_2S decomposition, requiring higher temperatures than CH_4 thermolysis, takes place after L=0.03, wherein CH_4 is decomposed completely. Most of the H_2S conversion occurs at the bottom half of the nozzle. The hydrogen mass fraction increases quickly at the top of the nozzle where CH_4 is decomposing. The slope of H_2 production would decrease when H_2S begins to decompose. The difference is

caused by the molar amount of produced H_2 in the chemical reaction. Fig. 8 shows that the feed gas enters the nozzle, carbon production starts with CH_4 cracking and reaches to a maximum value at about L=0.03,

then as H_2S is decomposed and S_2 is produced, carbon and S_2 react with each other and carbon mass fraction decreases due to formation of CS_2.
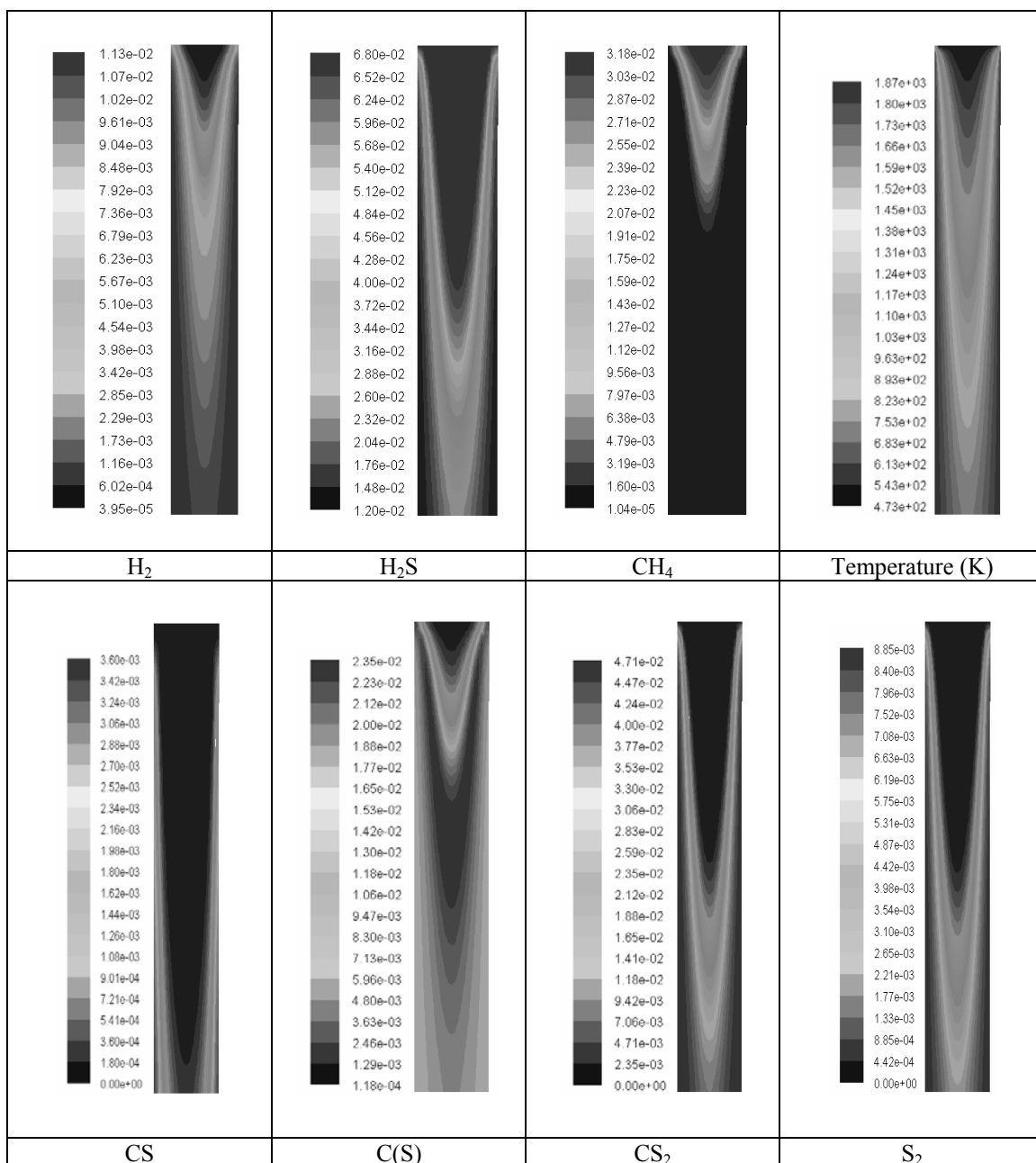

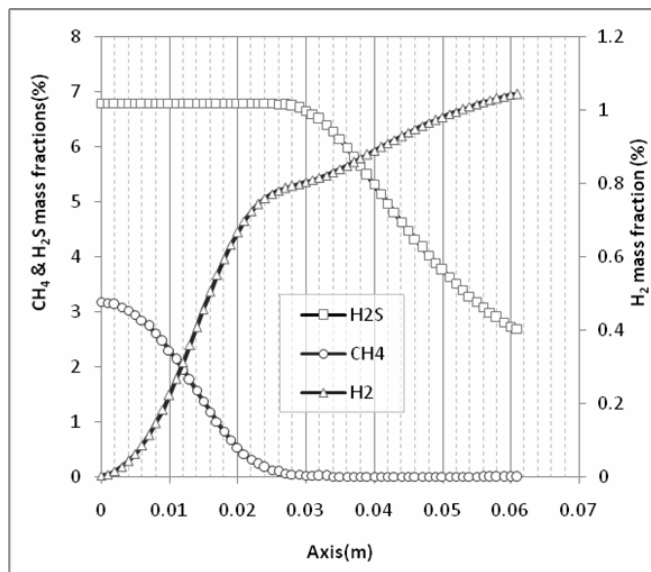**Figure 6.** Contours of temperature and species mass fraction in the nozzle H_2S/CH_4 ratio

Figure 7. Predicted mass fractions of H_2S, CH_4, and H_2 on the reactor axis
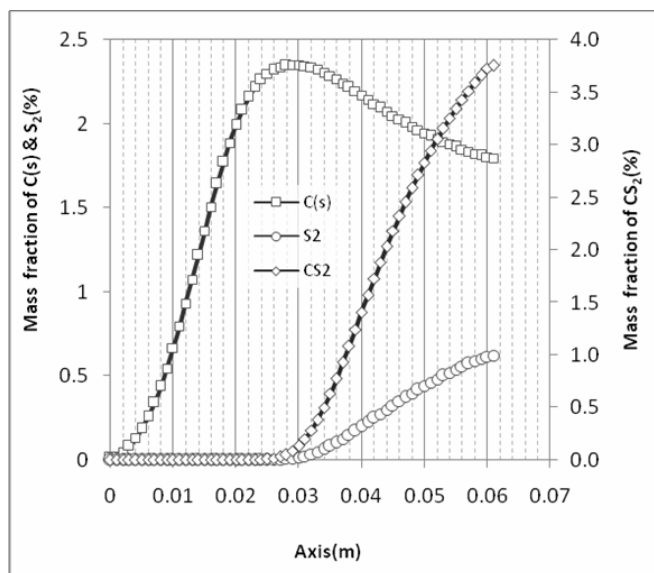

Figure 8. Predicted mass fractions of C(s), S_2, and CS_2 on the reactor axis

In Fig. 9 it is observed that lower mass fractions of CH_4 at the inlet mixture lead to higher temperatures. Since CH_4 has a lower pyrolysis temperature than H_2S, its decomposition starts rapidly and absorbs a significant amount of heat from the reactor. When CH_4 decreases at the inlet, the temperature increases due to reduction of the absorbed heat by methane decomposition. Therefore, the H_2S conversion rises and the increase in temperature slope is decelerated when H_2S/CH_4 ratio is higher than 5.

The effects of H_2S/CH_4 ratio on the average temperature of the nozzle and formation of different species have been considered.
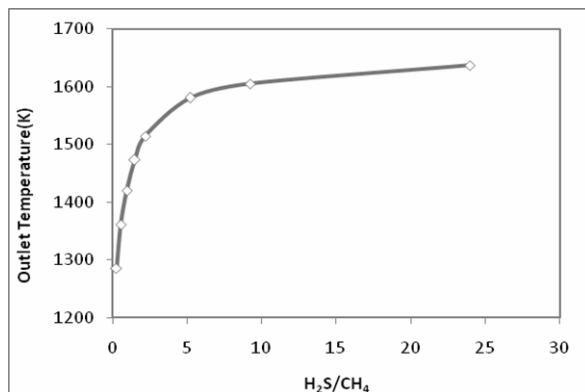
**Figure 9.** Predicted outlet temperature of the nozzle (on centerline) versus H_2S to CH_4 ratio

In Fig. 10 the yield of H_2 decreases along with CH_4, and H_2S increase. On the other hand, for H_2S/CH_4 ratios higher than 2 the temperature increases with the reduction of decomposition of CH_4, therefore H_2 yield increases. The yield of H_2 reaches to a maximum and then decreases slightly due to almost constant reactor temperature.
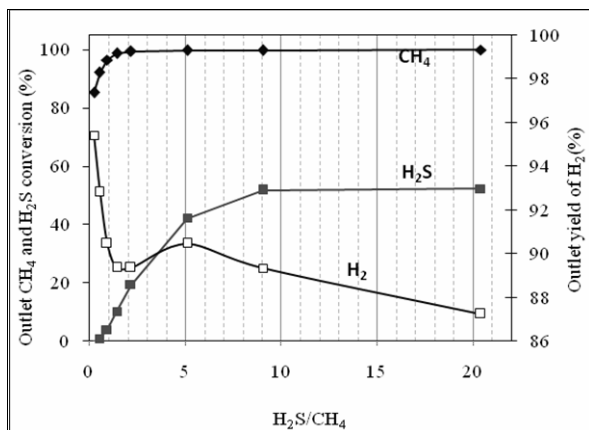
Figure 10. Effects of H_2S/CH_4 in feed gas on H_2S and CH_4 conversion and H_2 yield in center of outlet

Fig. 11 demonstrates the effects of H_2S to CH_4 ratio on the yield of C, S_2, and CS_2, respectively. Also, it can be seen that CS_2 yield increases with increasing H_2S to CH_4 ratio until it reaches a peak, and then drops with further increase in H_2S in the feed gas

flow rate. Although the H_2S to CH_4 ratio increases, CS_2 decreases after $H_2S/CH_4=5$.
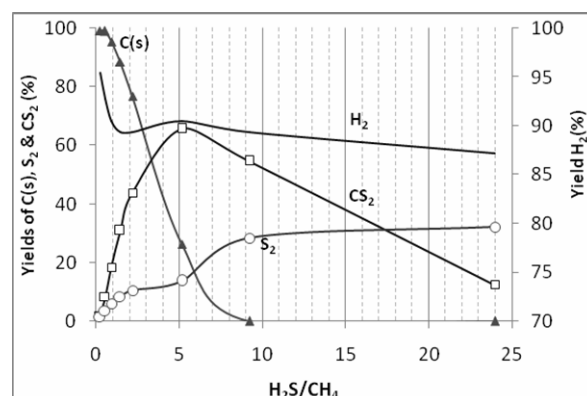
Figure 11. Effects of H2S to CH4 ratio in feed gas on C(s), S2, H2, and CS2 yields in center of outlet

6. Conclusions
The production of hydrogen from sour natural gas containing methane (CH_4) and hydrogen sulfide (H_2S) inside a solar reactor, used by Abanades, has been discussed. Based on the presented results, the following conclusions may be drawn:

- The main factor influencing CH_4 and H_2S conversions is reactor temperature. Due to the different decomposition temperatures of CH_4 and H_2S, the results show complex behavior in the products formation.

- In low H_2S/CH_4 ratios the temperature increases sharply by increasing the ratio, due to decrease in CH_4 decomposition.

- With increasing H_2S to CH_4 ratio in the feed gas, the CH_4 and H_2S conversions rise to approach a constant value, because of the reactor temperature variations.

- The production of H_2 from pure natural gas (CH_4) decomposition has the highest efficiency. By increasing H_2S mass

fraction in the feed gas, the yield of H_2 decreases sharply to the minimum value where the H_2S/CH_4 ratio is around 2. Further increase in H_2S mass fraction, and the reactor temperature as a result, increases H_2 production to its maximum value at $H_2S/CH_4=5$.

- CS_2 yield reaches its global maximum value at H_2 corresponding to local maximum.

- CS_2 production uses S_2 and solid carbon species in the reactor, which causes a sudden change in the increasing trend of S_2 yield.

References

[1] Ryu, H., Lee, Y., Lee, H., Han, Y., Lee, J., Yoon, J., Catalytic characteristics of various rubber-reinforcing carbon blacks in decomposition of methane for hydrogen production, J. Catalysis Today, 123, 303–309, (2007).

[2] Abdel, H. K., Shalabi, M. A., AL-Harbi, D. K. and Hakeem, T., Non-catalytic partial oxidation of sour natural gas, Int. J. Hydrogen Energy, 23, 457-462, (1998).

[3] T-Raissi, A., Paster, M. Analysis of solar thermochemical water-splitting cycles for hydrogen production, Progress Report, Florida Solar Energy Center, (2003).

[4] Gruenberger, T. M., Moghiman, M., Bowen, P. J., Syred, N., Dynamics of soot formation by turbulent combustion and thermal decomposition of natural gas, Combustion Science and Technology, 174, 67-86, (2002).

[5] Lambert, T. W., Goodwin, V. M., Stefani, D., Strosher, L., Hydrogen sulfide (H2S) and sour gas effects on the eye. A historical perspective, Int. J. Science of the Total Environment 367, 1–22 (2006).

[6] Abanades, S., Flamant, G. Experimental study and modeling of a high-temperature solar chemical reactor for hydrogen production from methane cracking, International Journal of Hydrogen Energy 32, 1508 – 1515(2007)

[7] Abanades, S., Flamant, G. Hydrogen production from solar thermal dissociation of methane in a high temperature fluid-wall chemical reactor, Chemical Engineering and Processing 47, 490–498, (2008)

[8] Rodat, S., Abanades, S., Couliéb, J., Flamant, G. Kinetic modeling of methane decomposition in a tubular solar reactor, Chemical Engineering Journal 146, 120–127(2009)

[9] Huang, C., T-Raissi, A., Thermodynamic analyses of hydrogen production from sub-quality natural gas, Part II: Steam reforming and autothermal steam reforming, J. Power Sources 163, 637–644 (2007).

[10] Ghosh, U., The Role of Black Carbon in Influencing Availability of PAHs in Sediments, J. Human and Ecological Risk assessment 13, 276-285 (2007).

[11] Petrasch, J., Steinfeld, A. Dynamics of a solar thermochemical reactor for steam-reforming of methane, J. Chemical Engineering Science 62, 4214-4228 (2007)

[12] Towler, P., Lynn, S., Sulfur recovery with reduced emissions, low capital investment and hydrogen co-production, J. Chemical engineering communications 155, 113-143 (1996).

[13] Dunker, A. M., Kumar, S., Mulawa, P. A., Production of hydrogen by thermal decomposition of methane in a fluidized-bed reactor-Effects of catalyst, temperature, and residence time, J. Hydrogen Energy 31, 473-484 (2006).

[14] Saario, A., Rebola, A. Heavy fuel oil combustion in a cylindrical laboratory furnace: Measurements and modeling, J. Fuel 84, 359–369 (2005).

[15] Murthy, J. Y. and Mathur, S. R., A finite volume method for radiative heat transfer using unstructured meshes, AIAA-98-0860 (1998).

[16] Yakhot, V., Orszag, S. Renormalization group analysis of turbulence. I. Basic theory. J. Scientific Computing 1, 3–51 (1986).