

**Research note**

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

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### **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<sub>4</sub> and H<sub>2</sub>S 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<sub>2</sub>) and a high-value nano-material of carbon. The effects of H<sub>2</sub>S to CH<sub>4</sub> feed ratio and reactor temperature on hydrogen, carbon black, S<sub>2</sub> and CS<sub>2</sub> formation are investigated. The results show complex behavior in the products because of the difference in CH<sub>4</sub> and H<sub>2</sub>S pyrolysis temperatures. It can be seen that for H<sub>2</sub>S/CH<sub>4</sub>>2, the yields of H<sub>2</sub> and CS<sub>2</sub> reach a local and global maximum at H<sub>2</sub>S/CH<sub>4</sub>=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<sub>4</sub> and H<sub>2</sub>S are considered as alternative sources of hydrogen [2, 3]. On the other hand, there is ample scope for CH<sub>4</sub> and H<sub>2</sub>S as the raw source of H<sub>2</sub>, because the

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energy required for CH<sub>4</sub> and H<sub>2</sub>S splitting ( $\Delta H_{\text{CH}_4}=74.9$  kJ/mol and  $\Delta H_{\text{H}_2\text{S}}=79.9$  kJ/mol) is much less than water splitting ( $\Delta H_{\text{water}}= 284.7$  kJ/mol) [4]. There are several convenient technologies for production of H<sub>2</sub> from CH<sub>4</sub>, 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<sub>2</sub>). In addition to the decrease in the required energy, the CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> emission occurs during the process [7,8]. Hydrogen sulfide (H<sub>2</sub>S) 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<sub>2</sub>S concentration in NG varies from traces to 90% by volume. In natural gas processing, H<sub>2</sub>S 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<sub>4</sub>+H<sub>2</sub>S produces hydrogen, carbon, and other sulfur compounds [6]. Therefore, the production of hydrogen by solar reactor has received 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<sub>2</sub> has high efficiency in CH<sub>4</sub> 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<sub>2</sub> 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].

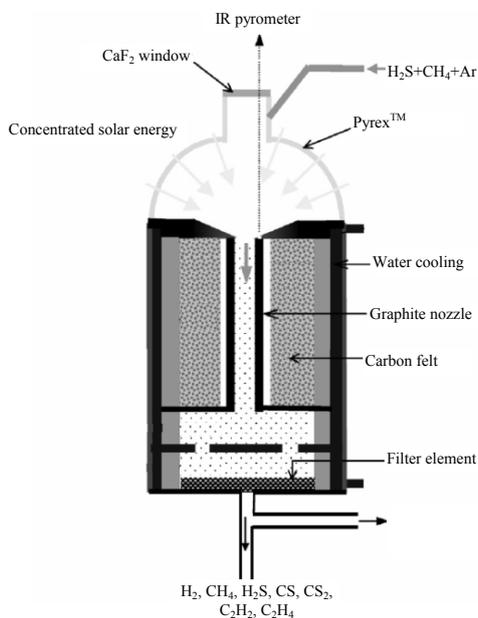
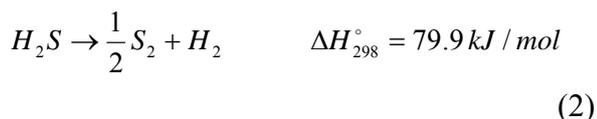
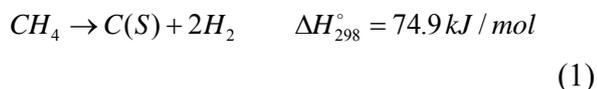


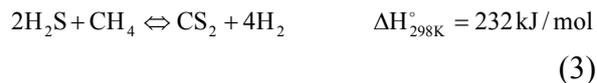
Figure 1. Solar reactor [6]

The gas flowing in the nozzle, positioned in the center of the reactor, is a mixture of Ar, CH<sub>4</sub>, and H<sub>2</sub>S. 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<sub>4</sub> and H<sub>2</sub>S as follows [3, 12]:



Reaction 1 requires temperatures higher than 850° K to proceed at reasonable rates [13] and in reaction 2 temperatures above

1500° K are required for achieving reasonable rates [9]. Thermodynamics of thermal CH<sub>4</sub> decomposition calculate that reaction (1) is complete at about 1300K [7]. Under special circumstances like using a catalyst, H<sub>2</sub>S can react with methane producing carbon disulfide (CS<sub>2</sub>) and H<sub>2</sub> [3].



The kinetic mechanisms of thermal CH<sub>4</sub> decomposition are stepwise dehydrogenation at high temperature (2CH<sub>4</sub>→C<sub>2</sub>H<sub>6</sub>→C<sub>2</sub>H<sub>4</sub>→C<sub>2</sub>H<sub>2</sub>→2C), which is included in the chemical reactions model of the reactor [7].

### 3. Turbulence–chemistry interaction

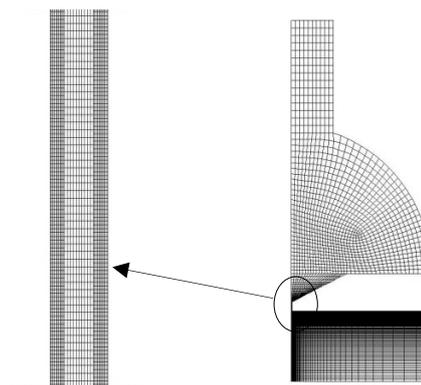
The Probability Density Function (PDF) method is used to model the turbulent chemical reactions occurring in the diffusion, combustion, and thermal decomposition of natural gas in the carbon black furnace. This method, which assumes the chemistry is fast enough for a chemical equilibrium to always exist 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- $\epsilon$  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<sub>4</sub> and H<sub>2</sub> concentration profiles, and conversion rates as a function of process parameters.

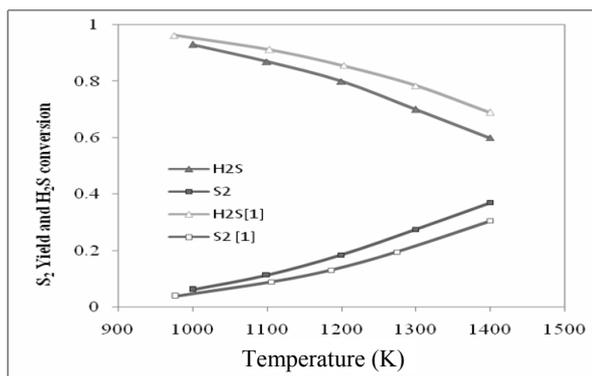


**Figure 2.** Two-dimensional quadrilateral grid of reactor model

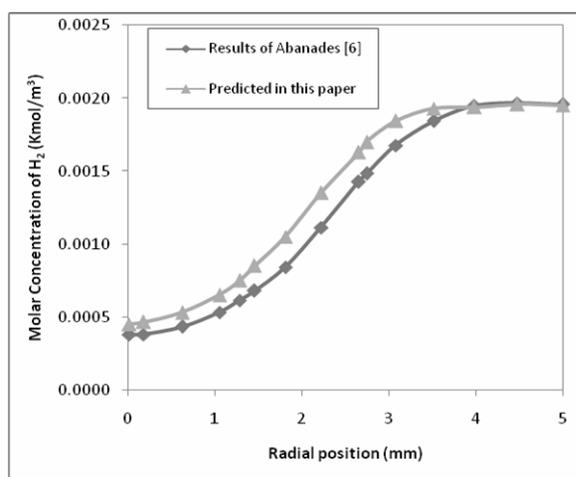
#### 5. Results and discussion

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<sup>2</sup> is assumed to be imposed to the inner walls of the nozzle. The results with pure CH<sub>4</sub> and a mixture of CH<sub>4</sub> and H<sub>2</sub>S feed gas are compared with the results of Abanades [6] and Towler & Lynn [12], respectively. A comparison between the H<sub>2</sub>S conversion and S<sub>2</sub> 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<sub>2</sub> in radial direction from the nozzle axis in Fig. 4. The molar concentration of H<sub>2</sub> 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]

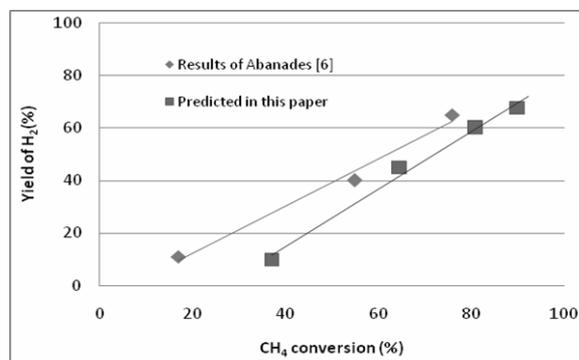


**Figure 4.** Comparison of molar concentration of  $H_2$  with the result of Abanades [6]

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  $CS_2$ .

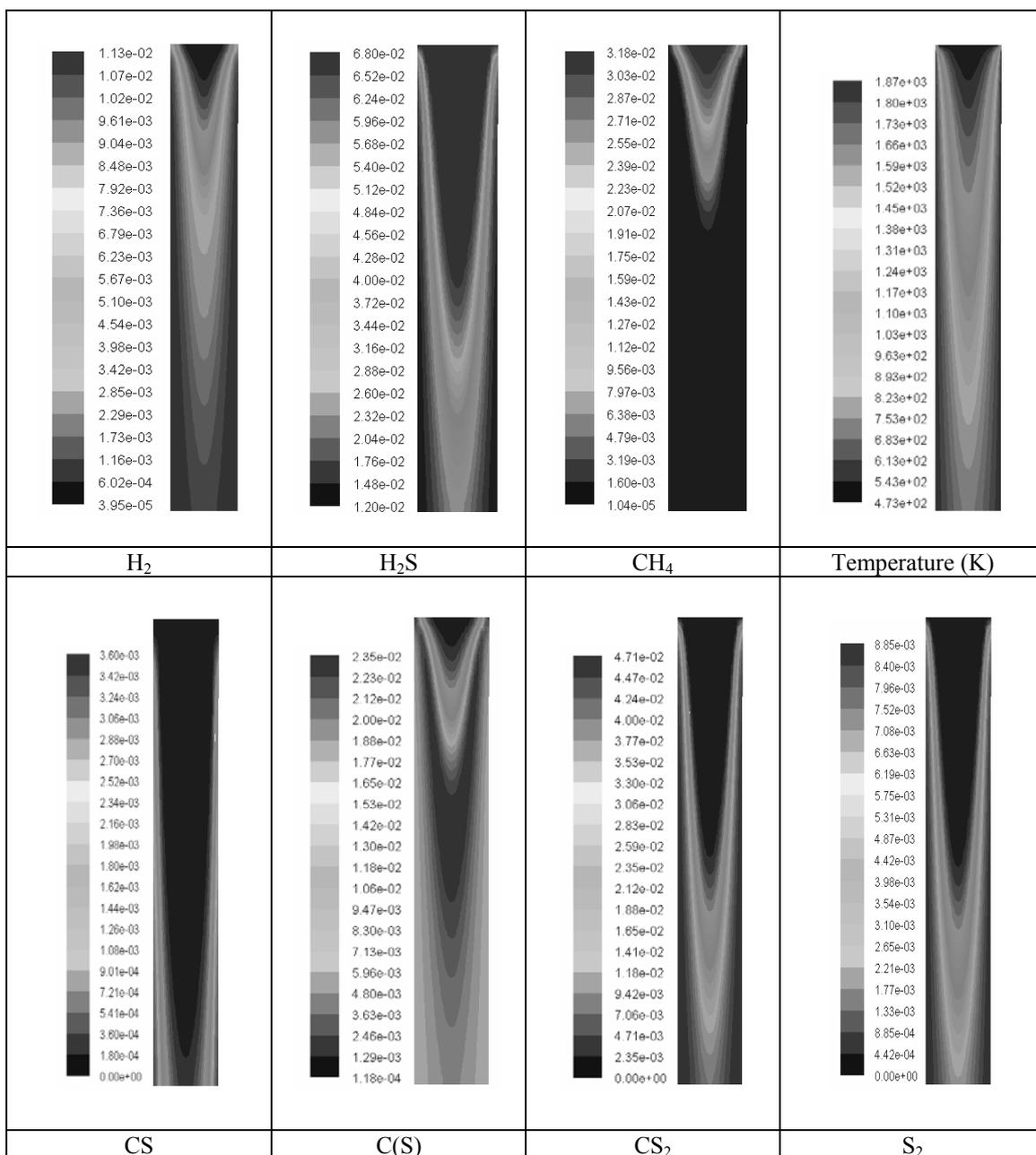


Figure 6. Contours of temperature and species mass fraction in the nozzle  $H_2S/CH_4$  ratio

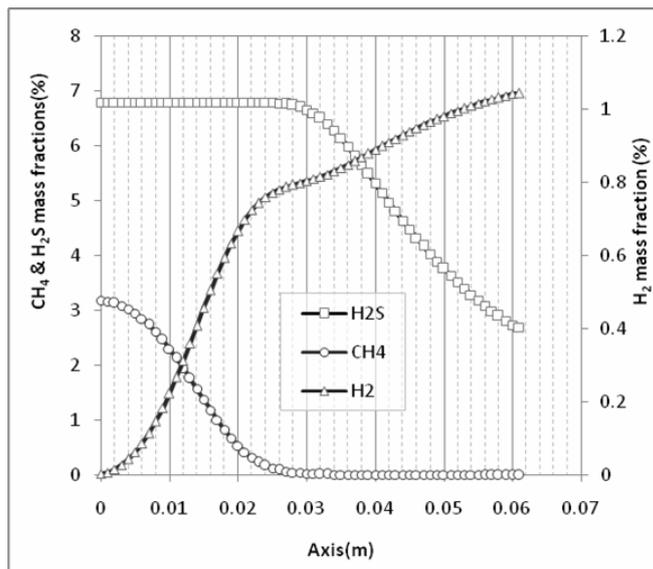


Figure 7. Predicted mass fractions of H<sub>2</sub>S, CH<sub>4</sub>, and H<sub>2</sub> on the reactor axis

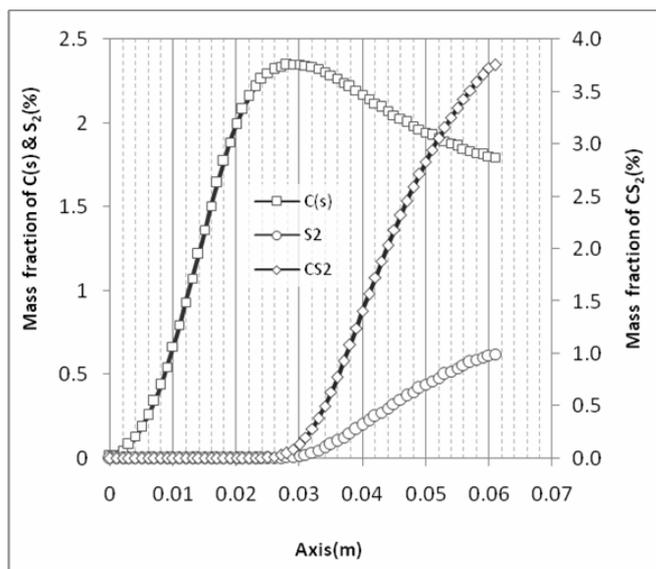
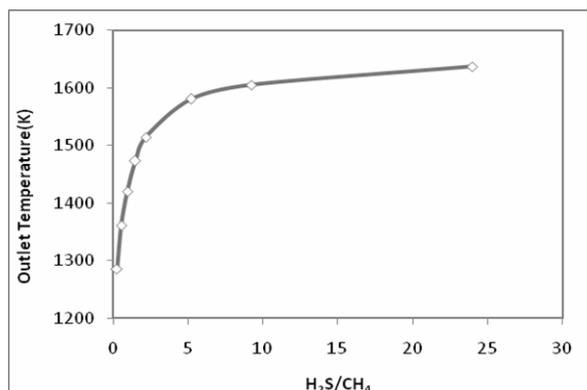


Figure 8. Predicted mass fractions of C(s), S<sub>2</sub>, and CS<sub>2</sub> on the reactor axis

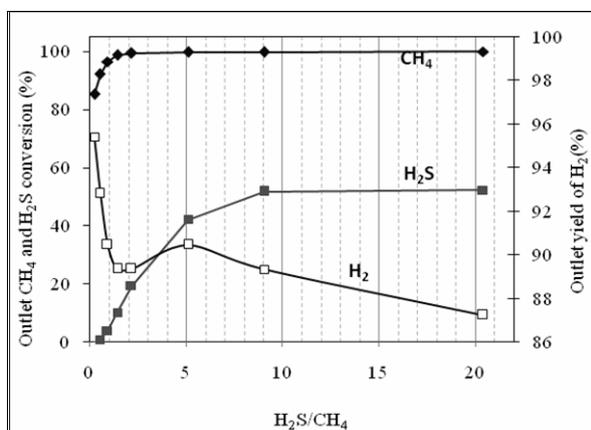
In Fig. 9 it is observed that lower mass fractions of CH<sub>4</sub> at the inlet mixture lead to higher temperatures. Since CH<sub>4</sub> has a lower pyrolysis temperature than H<sub>2</sub>S, its decomposition starts rapidly and absorbs a significant amount of heat from the reactor. When CH<sub>4</sub> decreases at the inlet, the temperature increases due to reduction of the

absorbed heat by methane decomposition. Therefore, the H<sub>2</sub>S conversion rises and the increase in temperature slope is decelerated when H<sub>2</sub>S/CH<sub>4</sub> ratio is higher than 5. The effects of H<sub>2</sub>S/CH<sub>4</sub> 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<sub>2</sub>S to CH<sub>4</sub> ratio

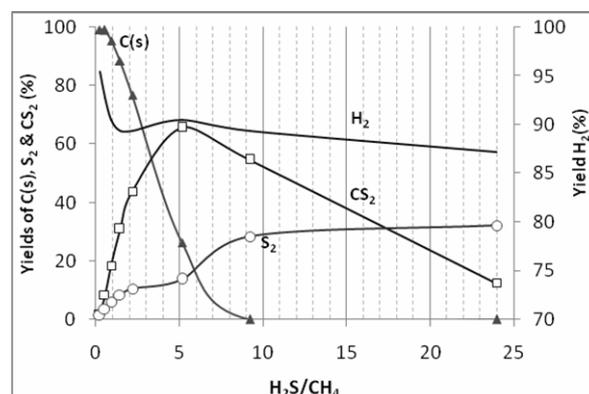
In Fig. 10 the yield of H<sub>2</sub> decreases along with CH<sub>4</sub>, and H<sub>2</sub>S increase. On the other hand, for H<sub>2</sub>S/CH<sub>4</sub> ratios higher than 2 the temperature increases with the reduction of decomposition of CH<sub>4</sub>, therefore H<sub>2</sub> yield increases. The yield of H<sub>2</sub> reaches to a maximum and then decreases slightly due to almost constant reactor temperature.



**Figure 10.** Effects of H<sub>2</sub>S/CH<sub>4</sub> in feed gas on H<sub>2</sub>S and CH<sub>4</sub> conversion and H<sub>2</sub> yield in center of outlet

Fig. 11 demonstrates the effects of H<sub>2</sub>S to CH<sub>4</sub> ratio on the yield of C, S<sub>2</sub>, and CS<sub>2</sub>, respectively. Also, it can be seen that CS<sub>2</sub> yield increases with increasing H<sub>2</sub>S to CH<sub>4</sub> ratio until it reaches a peak, and then drops with further increase in H<sub>2</sub>S in the feed gas

flow rate. Although the H<sub>2</sub>S to CH<sub>4</sub> ratio increases, CS<sub>2</sub> decreases after H<sub>2</sub>S/CH<sub>4</sub>=5.



**Figure 11.** Effects of H<sub>2</sub>S to CH<sub>4</sub> ratio in feed gas on C(s), S<sub>2</sub>, H<sub>2</sub>, and CS<sub>2</sub> yields in center of outlet

## 6. Conclusions

The production of hydrogen from sour natural gas containing methane (CH<sub>4</sub>) and hydrogen sulfide (H<sub>2</sub>S) 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<sub>4</sub> and H<sub>2</sub>S conversions is reactor temperature. Due to the different decomposition temperatures of CH<sub>4</sub> and H<sub>2</sub>S, the results show complex behavior in the products formation.
- In low H<sub>2</sub>S/CH<sub>4</sub> ratios the temperature increases sharply by increasing the ratio, due to decrease in CH<sub>4</sub> decomposition.
- With increasing H<sub>2</sub>S to CH<sub>4</sub> ratio in the feed gas, the CH<sub>4</sub> and H<sub>2</sub>S conversions rise to approach a constant value, because of the reactor temperature variations.
- The production of H<sub>2</sub> from pure natural gas (CH<sub>4</sub>) decomposition has the highest efficiency. By increasing H<sub>2</sub>S mass

fraction in the feed gas, the yield of H<sub>2</sub> decreases sharply to the minimum value where the H<sub>2</sub>S/CH<sub>4</sub> ratio is around 2. Further increase in H<sub>2</sub>S mass fraction, and the reactor temperature as a result, increases H<sub>2</sub> production to its maximum value at H<sub>2</sub>S/CH<sub>4</sub>=5.

- CS<sub>2</sub> yield reaches its global maximum value at H<sub>2</sub> corresponding to local maximum.
- CS<sub>2</sub> production uses S<sub>2</sub> and solid carbon species in the reactor, which causes a sudden change in the increasing trend of S<sub>2</sub> yield.

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