



Numerical investigation of hydrogen production inside a solar chemical reactor from sour natural gas

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Abstract

There is ample scope for CH₄ and H₂S as the raw source of H₂ production. CH₄ and H₂S splitting requires a very less energy compared to water splitting. The objective of this paper is investigation of the hydrogen production through thermal decomposition of waste gases containing CH₄ and H₂S inside a solar reactor. In this study a solar reactor has been applied to absorb solar power and allow it to concentrate in a graphite nozzle in the middle of reactor then transfer it to a flow reactant. The main issue from the economical standpoint is the production of valuable products hydrogen. The results show that the factor influencing H₂ production is H₂S to CH₄ ratio feed gas. Also, the reactor temperature as a function of H₂S/CH₄ ratio feed gas, increase precipitously with increasing H₂S/CH₄ feed gas ratio due to the mildly endothermic nature of CH₄ (H₂S decomposition is highly endothermic). For average wall reactor temperatures higher than 1600 k, the reactor CH₄ conversion reaches 100%, whilst H₂S conversion reach a reasonable rate in temperatures higher than 1300 k.

Keywords: Hydrogen, thermal decomposition, sour natural gas, solar reactor

Introduction

Scientists promote hydrogen as potential fuel for motive power (including cars, boats and airplanes), the energy needs of buildings and portable electronics. Hydrogen is a talented candidate as an ideal and clean source of energy [1]. Futurists believe a hydrogen economy could greatly reduce the emission of carbon dioxide and therefore play a major role in tackling global warming. Countries without oil, but with renewable energy resources, could use a combination of renewable energy and hydrogen instead of fuels derived from petroleum, which are becoming scarcer, to achieve energy independence.

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]. Although water is an ideal hydrogen source, CH₄ and H₂S could become alternative source of hydrogen [2, 3]. On the other hand, there is ample scope for CH₄ and H₂S as the raw source of H₂, because CH₄ and H₂S splitting ($\Delta H_{CH_4} = 74.9 \text{ kJ/mol}$ and $\Delta H_{H_2S} = 79.9 \text{ kJ/mol}$) requires a very less energy compared to water splitting ($\Delta H_{water} = 284.7 \text{ kJ/mol}$) [4]. There are several conventional technologies for production of H₂ from CH₄, including steam methane reforming (SMR), partial oxidation and pyrolysis [5]. Methane decomposition is a moderately endothermic reaction. It requires a very less thermal energy (only 37.8 kJ per mol of hydrogen produced) compared to SMR (69 kJ/mol H₂). In addition to reduction of the required energy, the CO₂ emission will decrease in decomposition method [6]. The methane, which is the main component of high quality natural gas, can be decomposed to hydrogen and carbon black in the solar reactor [6].

As main positivist impacts, energy carrier H₂ produced with renewable energy and it is not contaminated by combustion by-products. Furthermore solar energy is stored as a transportable fuel in this study and no CO₂ emission occurs during the process [7, 8].

Hydrogen sulfide (H₂S) is a common contaminant in many of the world's natural gas (NG) wells. Approximately one-third of US NG resources can be considered as low or sub-quality gas not suited for pipeline shipment [9]. H₂S concentration in NG varies from traces to 90% by volume. In natural gas processing H₂S is viewed as a pollutant because it corrodes pipelines and deactivates metal-based catalysts used in steam methane reformation (SMR). Clearly this is of considerable concern in terms of global resource utilization and climate change implications. Gas flaring has also been blamed for environmental and human health problems such as acid rain, asthma, skin and breathing diseases [10].

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As mentioned above, production of hydrogen from SQNG is a feasible option utilizing this untapped energy resource while at the same time reducing carbon oxides and hydrogen sulfide emissions. In a solar reactor, thermal decomposition of $\text{CH}_4 + \text{H}_2\text{S}$ produces hydrogen, carbon and other sulfur compounds [6].

For the reasons that mentioned above, the production of Hydrogen by solar reactor has been considered recently. Petrasch et al have studied hydrogen production process using solar reactors with (by) SMR method [11]. Also Abanades have 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. According to the benefits of thermal decomposition method rather steam methane reformation method, in this paper the hydrogen production process from sour gasses has been studied using the proposed solar reactor by Abanades[6].

Chemical reaction modeling

The chemical reaction occurs in a reactor receiving solar energy as an 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]. 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 concentrates in graphite nozzle.

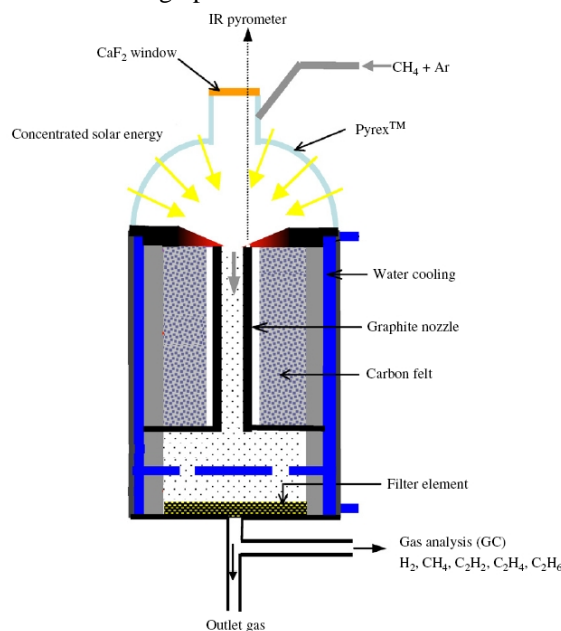
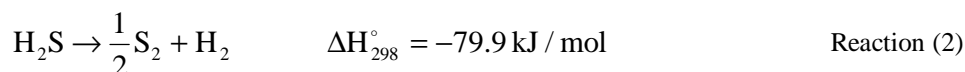
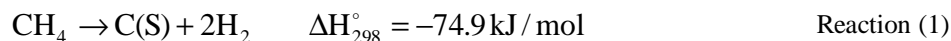


Fig.1. Solar reactor

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]:



Since reaction 1 is mildly endothermic, it requires temperatures higher than 850°K to proceed at reasonable rates [13], and, as reaction 2 is highly endothermic, temperatures in excess of 1500°K are required for achieving reasonable rates [9]. A portion of CH_4 and H_2S can oxidize to produce CO , CO_2 and SO_2 . H_2S can also react with CO_2 producing COS [14]:



Under special circumstances including using catalyst H_2S can react with methane producing carbon disulfide (CS_2) and H_2 [3].



Turbulence–chemistry interaction

The mixture fraction / 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 intermediate species. Transport equations are solved for the mean mixture fraction \bar{f} , its variance $\overline{f'^2}$ and for enthalpy \bar{h} . Calculations and PDF integrations are performed using a preprocessing code, assuming chemical equilibrium between 30 different species. The results of the chemical equilibrium calculations are stored in look-up tables which relate the mean thermo chemical variables (species mass fractions, temperature and density) to the values of \bar{f} , $\overline{f'^2}$ and \bar{h} [15].

Numerical solution procedure

The solar reactor used in this investigation is a reactor identical to that reported previously by Abanades [6]. The reactor has been simulated by a 2D axi-symmetrical model using a CFD software Fluent6.3. It has been used to model the reactor employing solution-adaptive grid refinement technique to solve the 2D problem. The 2D volume grid is represented in Fig 2. The domain is discretized into a grid of 9536 nodes and 9225 quadrilateral cells. The conservation equations for mass, momentum, energy, Reynold's stresses, dissipation rate, mixture fraction and its variance using a second-order upwind scheme for discretisation of the convective terms in the transport equations have been solved.

This model accounting for fluid flow mechanics, heat transfers (conduction, convection), mass transfers, and chemical reaction 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 rate as a function of process parameters.

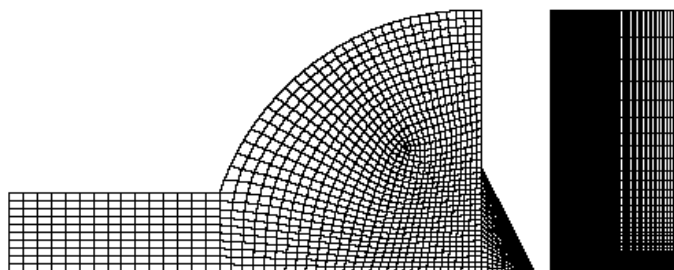


Fig. 2. Two-dimensional tetrahedral grid

Results

Numerical calculations were performed on the flow gas reactor described by Abonden [6] as shown in Fig. 1. The total reactor inlet airflow rate is 80 lit/hr, at a temperature of 473° K and pressure of 1 bar. The accuracy of the quantitative or even the qualitative trends for the combustion and decomposition parameters depend on the accuracy with which the temperature and species concentration fields are determined from the numerical calculation of the present model. To establish the accuracy of our model, The results have been calculated and compared with the results of Abanades [6], and Tawler & Lynn [12], with pure CH_4 and H_2S feed gas, respectively. A comparison of H_2S conversion and S_2 yield predicted by this model and experimental results [12] is given in Figs. 3. Resulting of Fig. 3 show that the predicted H_2S conversion and S_2 yields and results of Tawler and Lynn[12] are in very good agreement. Another validation has been performed on molar concentration of H_2 to radial distance from axis in Fig. 4. The molar concentration of H_2 increases from the center to the graphite nozzle heated by concentrated solar energy.

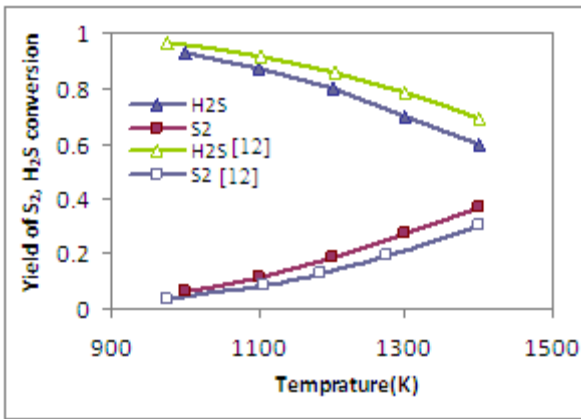


Fig 3. Comparison of the predicted yields of S₂ and H₂S conversion with the result of Tawler and Lynn [12]

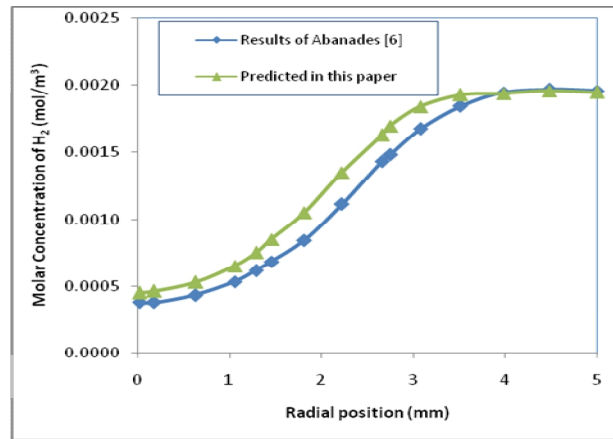


Fig 4. Comparison of the predicted yield of H₂ with the result of Abanades [6]

At first formation process of different species inside the nozzle for 80 lit/hr flow rate at the inlet has been studied, the mass fraction of Argon is 0.9 in feed gas and H₂S/CH₄=1, then the effect of H₂S/CH₄ on producing of different species has been considered. The mass fraction of produced species and temperature distribution in the nozzle has been represented in Fig 5. As it has been shown in Fig. 5 CH₄ decomposition reaction begins at near position to the inlet of nozzle rather H₂S.

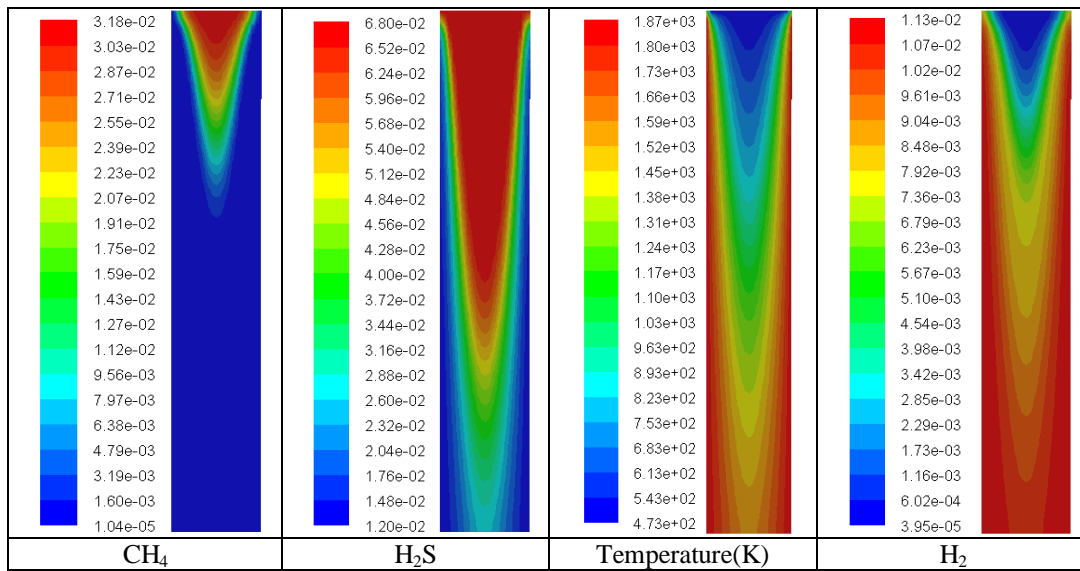


Fig. 5. Contour of species mass fractions and temperature (K)

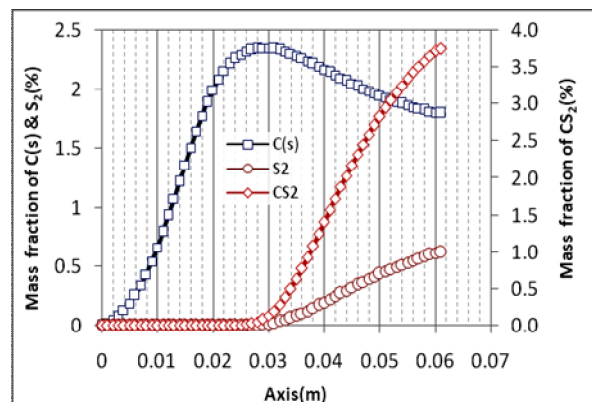
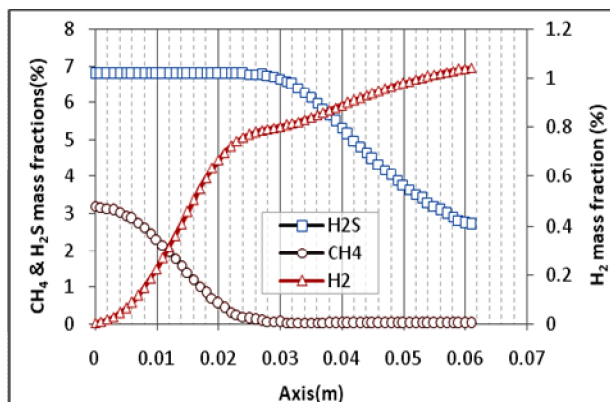




Fig. 6. Predicted mass fractions of H_2S , CH_4 and H_2 on axis of reactor

Fig. 7. Predicted mass fractions of $C(s)$, S_2 and CS_2 on axis of reactor

The variation of CH_4 , H_2S , H_2 , $C(s)$, S_2 and CS_2 mass fraction to Axial position has been depicted in Figs.6 and 7. CH_4 mass fraction is maximum in the inlet of the nozzle, it decomposes by passing through the nozzle quickly so that CH_4 is converted completely at $L=0.03$. Since methane decomposition is an endothermic reaction, the mixture temperature decreases. As a result H_2S required higher temperature than CH_4 , does not decomposed simultaneously with CH_4 . Most of the H_2S conversion occurs at the bottom half of the nozzle. Thus mass fraction of Hydrogen increases rapidly in the top half of the nozzle than the bottom half in which H_2S is decomposed. Fig.7 depicts as feed gas enters the nozzle, Carbon production starts with CH_4 cracking, it reaches to greatest extent at about $L=0.03$, then as H_2S decomposed and S_2 is produced. carbon and S_2 react together, So CS_2 is formed and Carbon mass fraction decreases. The effect of H_2S/CH_4 ratio on average temperature of the nozzle and formation of different species has been considered. A constant heat flux of $15000W/m^2$ is imposed to the nozzle. As it has been shown in Fig.9, the lower mass fraction of CH_4 at the inlet mixture, the higher temperature. Since CH_4 has a low pyrolysis temperature than H_2S , its decomposition starts rapidly and absorbs a high heat of the reactor. When CH_4 decreases at the inlet, the temperature increases due to decrease of absorbed heat for methane decomposition. Therefore the H_2S conversion raises (Fig. 8), so that the increase rate of the temperature reduces when H_2S/CH_4 ratio is higher than 5. At first of the Fig. 8 H_2 yield decreases along with lessening CH_4 and increasing of H_2S . as a result H_2S conversion and H_2 yield increases. The yield of H_2 reaches to maximum. Then H_2 yield decreases slightly due to not many differences in the reactor temperature.

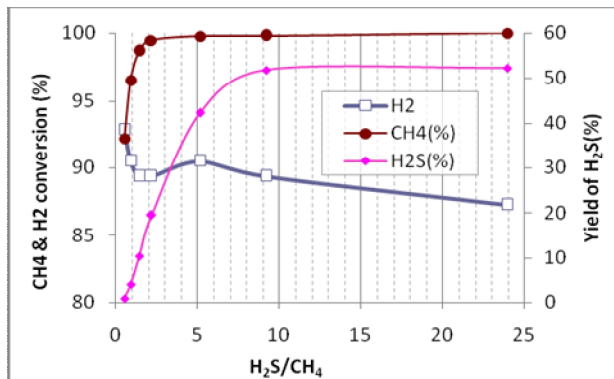


Fig. 8. Predicted mass fractions of $C(s)$, S_2 and CS_2 on axis of reactor

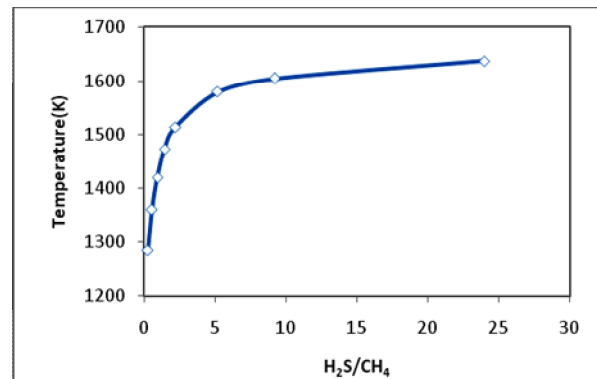


Fig. 9. Predicted temperature of the nozzle to H_2S/CH_4

Figs. 9 and 10 depict the effects of H_2S to CH_4 ratio and temperature on the yield of C , S_2 and CS_2 , respectively, Fig. 10 shows that CS_2 yields increase with increased H_2S to CH_4 ratio until they reach a peak, and then drop with further increase in feed gas flow rate.

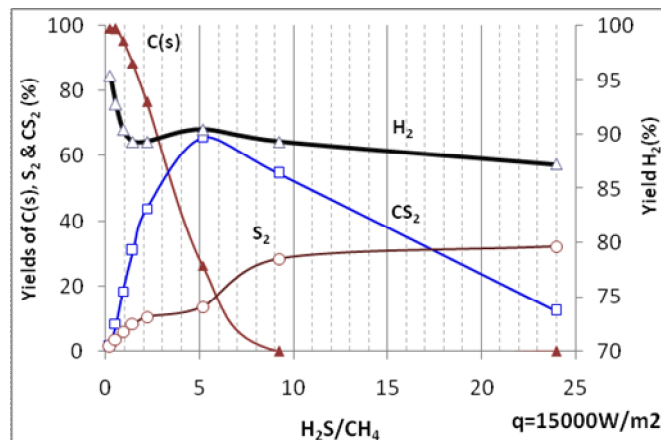


Fig. 10. Effect of H_2S to CH_4 ratio feed gas on $C(s)$, S_2 , H_2 and CS_2 yields

Conclusions



The production of hydrogen black from sub-quality natural gas containing methane (CH_4) and hydrogen sulfide (H_2S) inside a solar reactor has been analyzed. The process involved the thermal decomposition of CH_4 and H_2S . Based on the presented results, the following conclusions may be drawn:

- In the constant heat flux, the major factor influencing H_2 yield is H_2S to CH_4 ratio feed gas.
- The yield of hydrogen for sour natural gas, in $\text{H}_2\text{S}/\text{CH}_4=5$ is maximum.
- For H_2S to CH_4 ratio higher than 5, CS_2 formation decreases sharply with $\text{H}_2\text{S}/\text{CH}_4$.
- For $\text{H}_2\text{S}/\text{CH}_4=5$, the yields of H_2 and CS_2 are in maxima.

References

- [1] Ryu H, Lee Y, Lee H, Han Y, Lee J, Yoon J, *J. Catalysis Today*, 123, 303–309 (2007).
- [2] Abdel, H. K., Shalabi, M. A., AL-Harbi D. K. and Hakeem T., *Int. J. Hydrogen Energy*, 23, 457-462 (1998).
- [3] Ali T-Raissi, Analysis of Solar Thermochemical Water-Splitting Cycles for Hydrogen Production
- [3] Huang, C., T-Raissi, A., *J. Power Sources*, 175, 464-472 (2008).
- [4] Gruenberger, T. M., Moghiman, M., Bowen, P. J., Syred, N., *Combust. J. Sci. and Tech.*, 174, 67-86, (2002).
- [5] Lambert, T. W., Goodwin, V. M., Stefani, D., Strosher, L., *Int. J. Science of the Total Environment*, 367, 1–22 (2006).
- [6] S. Abanades, G. Flamant, Experimental study and modeling of a high-temperature solar chemical reactor for hydrogen production from methane cracking, *International Journal of Hydrogen Energy* 32 (2007) 1508 – 1515
- [7] S. Abanades, G. Flamant, Hydrogen production from solar thermal dissociation of methane in a high-temperature fluid-wall chemical reactor, *Chemical Engineering and Processing* 47 (2008) 490–498
- [8] S. Rodat, S. Abanades, J. Couliéb, G. Flamant, Kinetic modeling of methane decomposition in a tubular solar reactor, *Chemical Engineering Journal* 146 (2009) 120–127
- [9] Huang, C., T-Raissi, A., *J. Power Sources*, 163, 637–644 (2007).
- [10] Ghosh, U., *J. Human and Ecological Risk assessment*, 13, 276-285 (2007).
- [11] J. Petrasch, A. Steinfeld, Dynamics of a solar thermochemical reactor for steam-reforming of methane, *Chemical Engineering Science*, 62, 4214-4228 (2007)
- [12] Towler, P., Lynn, S., *J. Chemical engineering communications*, 155, 113-143 (1996).
- [13] Dunker, A. M., Kumar, S., Mulawa, P. A., *J. Hydrogen Energy*, 31, 473-484 (2006).
- [14] Sakanishi, K., Wu, Z., Matsumura, A., Saito, I., *J. Catalysis Today*, 104, 94–100 (2005).
- [15] Saario, A., Rebola, A., *J. Fuel*, 84, 359–369 (2005).