

Thermodynamic analyses of hydrogen production from sub-quality natural gas

Part II: Steam reforming and autothermal steam reforming

Cunping Huang*, Ali T-Raissi

Florida Solar Energy Center, University of Central Florida, 1679 Clearlake Road, Cocoa, FL 32922-5403, United States

Received 25 January 2006; received in revised form 17 February 2006; accepted 22 February 2006

Available online 2 May 2006

Abstract

Part I of this paper analyzed sub-quality natural gas (SQNG) pyrolysis and autothermal pyrolysis. Production of hydrogen via direct thermolysis of SQNGs produces only 2 mol of hydrogen and 1 mol of carbon per mole of methane (CH_4). Steam reforming of SQNG (SRSQNG) could become a more effective approach because the processes produce two more moles of hydrogen via water splitting. A Gibbs reactor unit operation in the AspenPlus™ chemical process simulator was employed to accomplish equilibrium calculations for the SQNG + H_2O and SQNG + H_2O + O_2 systems. The results indicate that water and oxygen inlet flow rates do not significantly affect the decomposition of hydrogen sulfide (H_2S) at temperatures lower than 1000 °C. The major co-product of the processes is carbonyl sulfide (COS) while sulfur dimer (S_2) and carbon disulfide (CS_2) are minor by-products within this temperature range. At higher temperatures (>1300 °C), CS_2 and S_2 become major co-products. No sulfur dioxide (SO_2) or sulfur trioxide (SO_3) is formed during either SRSQNG or autothermal SRSQNG processes, indicating that no environmentally harmful acidic gases are generated.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Hydrogen; Sub-quality natural gas; SMR; Autothermal process; Hydrogen sulfide; Carbonyl sulfide

1. Introduction

Part (I) of this paper [1,2] reviewed in detail the potential technologies applicable for hydrogen production from SQNGs. However, none of these technologies would be cost-effective in terms of H_2 production using a purely thermal process. Two novel approaches, SQNG pyrolysis and SQNG autothermal pyrolysis, are herein proposed and analyzed, and the results indicate that no separation of H_2S from hydrocarbons is required prior to the SQNG processing. These two approaches would potentially be cost-effective processes for utilizing SQNG as a new resource for the production of H_2 and CS_2 . This conclusion is based upon the fact that H_2S can be treated as an inert gas during the SQNG process. The objective of Part (II) of this paper is to further explore the applicability of conventional technologies, namely steam methane reforming (SMR) and autothermal

steam reformation, for the SQNG processing. The significant finding of this study is that, compared to natural gas pyrolysis, SRM produces two more moles of H_2 through water splitting. In addition to the increased H_2 production, SMR is a highly endothermic process which can be used to more effectively absorb heat from a thermal energy source such as concentrated solar thermal source. As in Part (I), a Gibbs reactor unit operation in the AspenPlus™ chemical process simulator was applied as a thermodynamic analytic tool for equilibrium calculation of the SQNG + H_2O and SQNG + H_2O + O_2 systems. Based on the stability of H_2S during the SQNG pyrolysis or steam reformation of SQNG, a two-step H_2 production from SQNG is proposed and discussed. The catalyst deactivation issue is also examined in this discussion.

2. Steam reforming of SQNG (SRSQNG)

The compositions of SQNG applied in this paper are the same as in Part I (the Blackjack Creek SQNG field) with a

* Corresponding author. Tel.: +1 321 638 1505; fax: +1 321 638 1010.
E-mail address: chuang@fsec.ucf.edu (C. Huang).

10% H₂S concentration. The total carbon is calculated from the total hydrocarbons in SQNG, which is 110.10 kmol h⁻¹. The thermodynamic analyses are conducted under isothermal conditions, assuming that the inlet component mole flow rates are equal to their mole fractions. The inlet water flow rates are calculated based on the ratio of water to the total carbon moles (110.10 kmol h⁻¹), x (=H₂O/C). The ratio x is selected as: 0.25, 0.50, 0.75, 1.0, 1.5 and 2.0 corresponding to the mole flow rates of 27.25, 55.05, 82.58, 110.10, 165.15 and 220.20 kmol h⁻¹.

2.1. Equilibrium flow rates of methane, hydrogen and carbon

Fig. 1 demonstrates the mole flow rates of CH₄, H₂ and C with the reforming temperatures. CH₄ decomposition during SRSQNG is similar to that in SQNG pyrolysis. At temperatures above 850 °C, since all the hydrocarbons are consumed, the H₂ outlet rate remains constant. Compared to SQNG pyrolysis, which produces a maximum of 200 kmol h⁻¹ H₂, the H₂ production rate during the course of SRSQNG, because of water splitting, increases with the water inlet flow rate, and is greater than 200 kmol h⁻¹. However, when x is greater than 1.0, no significant increase in H₂ production was observed. When $x = 2.0$, the maximum H₂ output is about 300 kmol h⁻¹, indicating that only 100 kmol h⁻¹ of H₂ results from the splitting of water, representing about 50% of the total water inlet. Water conversion into H₂ increases with the decrease of water input, and reaches 100% when x is less than 1.0, suggesting that 1 mol of C in SQNG can only split 1 mol of water in SRSQNG for the production of H₂.

In order to preclude C coke production during SRSQNG, the ratio x must be controlled. It is observed that the carbon flow rate decreases with an increase in the water inlet flow rate. At a lower water flow rate ($x < 1.0$), carbon laydown occurs throughout the entire temperature range. Only when $x > 1.0$ and the temperature is greater than 900 °C does the carbon flow rate decrease to zero, indicating that there is no carbon produced during the course of SRSQNG. This feature is important to the reforming process for the prevention of catalyst deactivation.

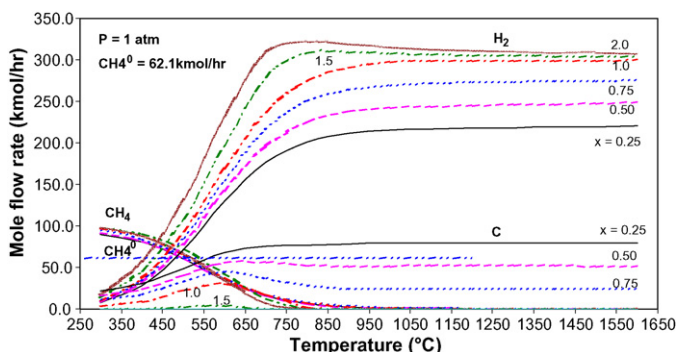


Fig. 1. Temperature dependence of equilibrium mole flow rates of CH₄, H₂ and C for SRSQNG ($x = \text{H}_2\text{O}/\text{C} = 0.25, 0.50, 1.0, 1.5$ and 2.0).

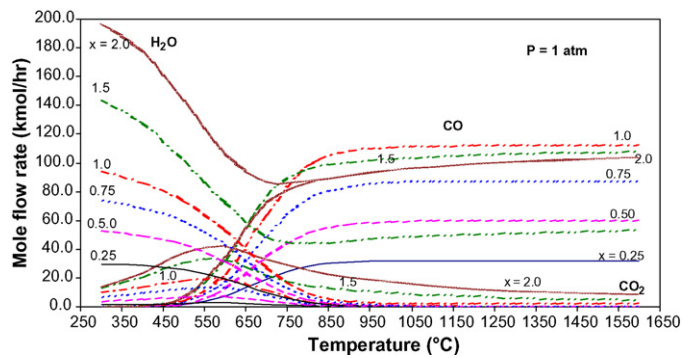


Fig. 2. Temperature dependence of equilibrium mole flow rates of H₂O, CO and CO for SRSQNG ($x = \text{H}_2\text{O}/\text{C} = 0.25, 0.50, 1.0, 1.5$ and 2.0).

2.2. Equilibrium flow rates of carbon dioxide, carbon monoxide and water

Equilibrium output flow rates of CO₂, CO and H₂O are shown in Fig. 2. The CO flow rate depends heavily upon H₂O input rate. CO flow rate reaches its maximum (~ 110 kmol h⁻¹) when $x = 1.0$, and then decreases as x increases further. During SRSQNG, CO₂ equilibrium flow rates do not significantly increase with water flow rate. Only when water flow rate is greater than 1.0 kmol h⁻¹ is CO₂ flow rate detectable in the outlet stream. Based on Figs. 1 and 2, the optimal H₂O to C ratio, x , should be set at 1.0 during the course of SRSQNG. Note that this number is deduced from the thermodynamic calculation and only presents an ideal ratio for SRSQNG.

2.3. Equilibrium flow rates of hydrogen sulfide, carbon disulfide and sulfur dimer

The equilibrium flow rates of H₂S at different x ratios are illustrated in Fig. 3. The initial mole fraction of H₂S is 10.0%, corresponding to 10.0 kmol h⁻¹ inlet to a Gibbs reactor in the AspenPlusTM chemical simulator.

H₂S conversion during SRSQNG is similar to that in SQNG pyrolysis. H₂S does not significantly decompose at different water input rates when temperature is lower than 1200 °C, indicating that it is stable and can be considered an inert gas within this temperature range. Even when temperature is as high as

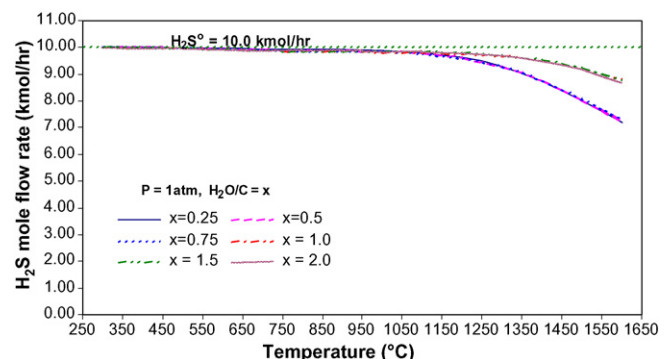


Fig. 3. Temperature dependence of equilibrium mole flow rates of H₂S for SRSQNG ($x = \text{H}_2\text{O}/\text{C} = 0.25, 0.50, 1.0, 1.5$ and 2.0).

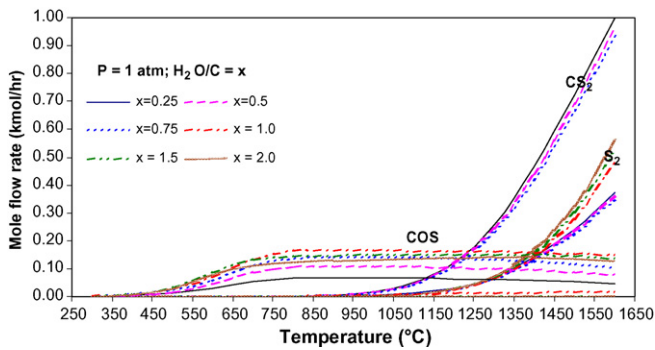


Fig. 4. Temperature dependence of equilibrium mole flow rates of COS, CS₂ and S₂ for SRSQNG ($x = \text{H}_2\text{O}/\text{C} = 0.25, 0.50, 1.0, 1.5$ and 2.0).

1600 °C, the decomposition increase is still less than 30%. Interestingly, at temperatures greater than 1200 °C, water influence on the H₂S conversion can be separated into two significant ranges: when $x < 1.0$, H₂S conversion is higher than that when $x > 1.0$, suggesting that higher water input favors the stability of H₂S. This may be attributed to the fact that higher H₂O inlet to the reactor generates a higher volume of H₂, thereby inhibiting the decomposition of H₂S. H₂O effect on the distribution of sulfur species is illustrated in Fig. 4.

The equilibrium flow rates of COS, CS₂ and S₂ are dependent upon both temperature and input H₂O flow rate and are shown in Fig. 4. No SO₂ or SO₃ exists in the equilibrium mixture, showing that SRSQNG does not produce sulfuric acid gas, and therefore no environmental impact exists in terms of SO₂ tail gas treatment. Since SRSQNG occurs at temperatures between 700 and 1000 °C, COS is a major byproduct at a low ppm level. The formation of COS is similar to the water gas shift process as indicated in the following reaction:



Since the output rate of CO depends on the input flow rate of H₂O, the COS production rate depends on water concentration. The maximum COS outlet rate occurs at $x = 1.0$ as a result of the increase in CO, as shown in Fig. 2. However, the difference in the COS production rates at various x levels is at insignificantly low levels (ppm range). Significant amounts of CS₂ can be observed when temperature exceeds 1200 °C. Fig. 4 indicates that the maximum CS₂ output flow rate occurs at a temperature of 1600 °C and is about 1.0 kmol h^{-1} , accounting for less than 0.4% of total output gases. CS₂ is produced according to H₂S methane reforming (HSMR) analogous to SMR:



Because SMR requires less energy than does Reaction (2), as indicated by comparative reactions between SMR and HSMR, the CS₂ production rate is heavily dependent upon the H₂O input rate. As shown in Fig. 4, when $x > 0.75$, the CS₂ output rate approaches zero. This is because that SMR becomes a major reaction producing a higher amount of CO, which reacts with H₂S to form COS (Reaction (1)).

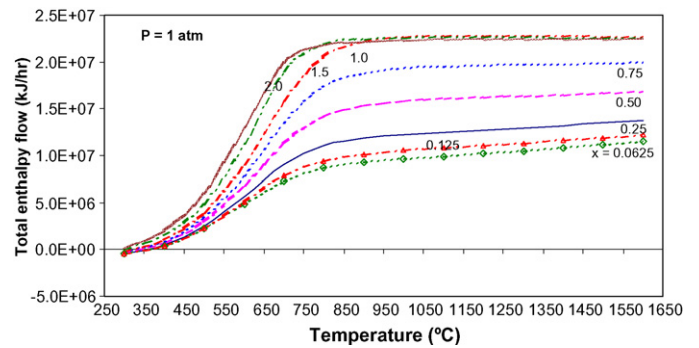


Fig. 5. Temperature dependence of total enthalpy for SQNGSR at different H₂O/C ratios ($x = \text{H}_2\text{O}/\text{C} = 0.0625, 0.125, 0.25, 0.50, 1.0, 1.5$ and 2.0).

S₂ is produced from the decomposition of H₂S based on:



Fig. 4 also shows that the decomposition of H₂S in the course of SRSQNG is more difficult than that in HSMR [3]. The very low S₂ output rate at temperatures lower than 1000 °C indicates, from a different angle, the stability of H₂S in SRSQNG. At low water inlet rates ($x < 1.0$) there is insignificant production of S₂. Only when x is greater than 1.0 do the rates slightly increase as x increases. The fact that S₂ production is at a much lower level than that of CS₂ in the higher temperature range is an indication that the H₂O effect on H₂S decomposition is insignificant.

2.4. Thermal energy requirement for SRSQNG processes

The heat requirements for SRSQNG depicted in Fig. 5 indicate that SRSQNG is a highly endothermic process. When x increases the total heat energy requirement increases significantly. However, when x is greater than 1.0, since no significant amount of H₂ is produced (Fig. 1), the heat requirements at these H₂O input rates are approximately the same. Combining the heat required for the production of H₂ by SRSQNG, shown in Figs. 1 and 5, we observe that a low x ratio requires less heat for production of 1 mol of H₂. The optimal x ratio for the heat requirement per mole of H₂ produced is $x = 1.0$.

3. Autothermal steam reforming of SQNG (autothermal SRSQNG)

As discussed above, SRSQNG is a highly endothermic process. To reduce the heat required from an external source, hydrocarbons in the SQNG can be burned internally to provide heat for the remaining hydrocarbon reforming. The aim of this analysis is to better understand the underlying chemistry in autothermal SRSQNG and to investigate the stability of H₂S in the presence of both water and oxygen. The other focus of this analysis is to determine if the process will produce sulfuric acid gases (SO₂ or SO₃). Two systems, SQNG + 0.0625H₂O + O₂ and SQNG + 0.25H₂O + O₂ are selected for investigating oxygen effects on autothermal SRSQNG. A low x ratio is selected for the analysis because SRSQNG at a low x value requires less

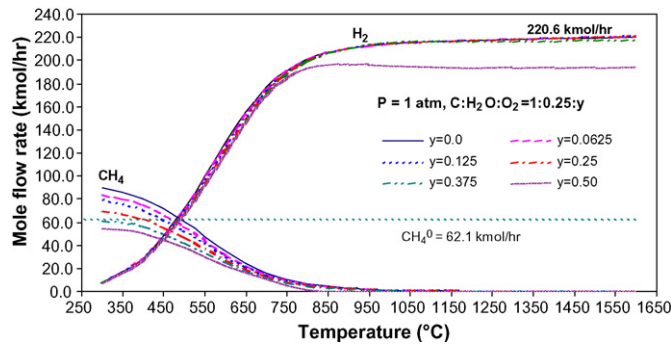


Fig. 6. Temperature dependence of CH₄ and H₂ flow rates at different oxygen inputs (C:H₂O:O₂ = 1:0.25:y).

heat to produce a given amount of H₂. The results obtained may also be applicable to a high x system. Through analysis it was found that two systems ($x = 0.0625$ and 0.25) have similar product equilibrium concentrations in the outlet stream. In order to keep the paper concise only the results for the $x = 0.25$ system are shown in this paper.

3.1. Equilibrium flow rates of methane, carbon and hydrogen during autothermal SRSQNG

Fig. 6 depicts equilibrium flow rates of CH₄ and H₂ at various inlet oxygen levels, with $x = 0.25$. As in the pyrolysis of SQNG, all other hydrocarbons are decomposed into H₂, CH₄ and carbon within a temperature range of 300–500 °C. The CH₄ flow rate decreases with increases of either temperature or oxygen flow rate. On the other hand, H₂ flow rates are independent of the oxygen input ratio when y ($=O_2/C$) is less than 0.375. When y increases to 0.50 the H₂ flow rate decreases slightly. The decrease is more significant at $x = 0.25$ than at $x = 0.0625$.

The temperature dependence of carbon deposition during autothermal SRSQNG is shown in Fig. 7. At a high water input ratio ($x = 0.25$), carbon lay down is greatly reduced as compared to a low ratio of x ($=0.0625$). At both water input rates carbon coking remains constant when the temperature is greater than 900 °C. When oxygen input flow rates increase, carbon lay down decreases. Zero coking occurs when y is greater than 0.5 for $x = 0.0625$ and 0.375 for $x = 0.25$, respectively. In other

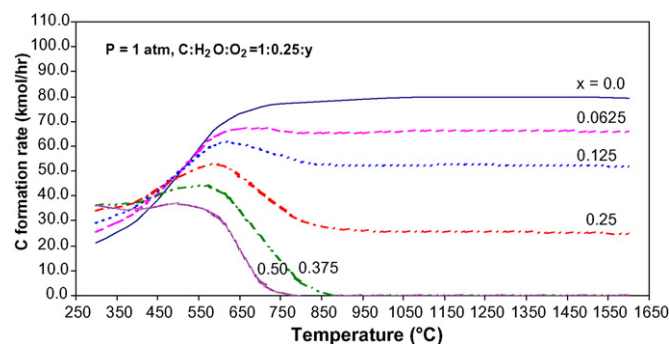


Fig. 7. Temperature dependence of carbon flow rates at different oxygen inputs (C:H₂O:O₂ = 1:0.25:y).

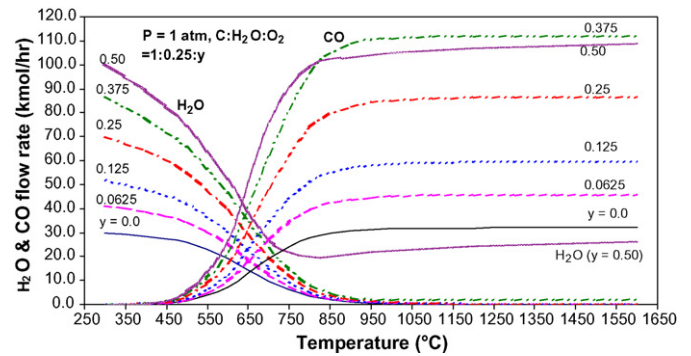


Fig. 8. Temperature dependence of CO and H₂O flow rates at different oxygen inputs (C:H₂O:O₂ = 1:0.25:y).

words, when the H₂O input flow rate increases, oxygen required to provide a zero coking condition is decreased.

3.2. Equilibrium flow rates of carbon monoxide, carbon dioxide and water during autothermal SRSQNG

Fig. 8 demonstrates the equilibrium flow rates of CO and H₂O during autothermal SRSQNG processes. The H₂O equilibrium flow rate increases with increasing oxygen inputs. However, the H₂O flow rate decreases as the temperature increases. At higher temperatures, H₂O reacts with CH₄ to produce H₂ and CO. Since CO can be shifted to H₂ and CO₂ through a water gas shift reaction; a higher CO output indicates more H₂ production. Combining Figs. 6 and 8 we can conclude that within certain water and oxygen input ranges an autothermal process does not reduce the H₂ production rate. However, note that when H₂O input is at a higher level (Fig. 8, $x = 0.25$), CO output at $y = 0.50$ is lower than that at $y = 0.375$. A similar result can be observed in the H₂ production rate shown in Fig. 6, suggesting that there exist optimal values of x and y for the production of H₂. Since the approach of an autothermal process is to oxidize part of the hydrocarbons in SQNG to produce heat for reforming the remaining CH₄, the extra oxygen input results in more hydrocarbons burned to produce CO₂, thereby leading to wasting hydrocarbons which could be used for the production of H₂. The CO₂ output flow rates are shown in Fig. 9. As discussed above, even though there is no significant increase in CO₂ outlet in the higher temperature range, with y less than

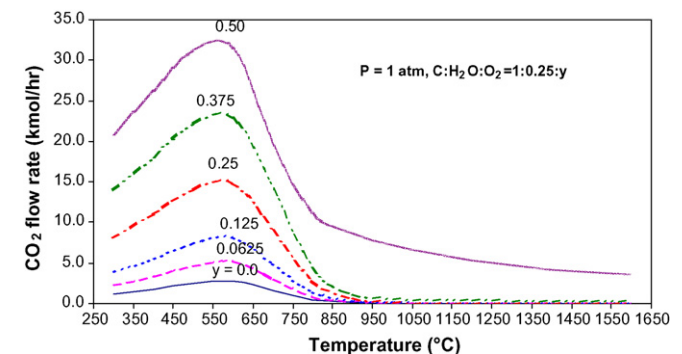


Fig. 9. Temperature dependence of CO₂ flow rates at different oxygen inputs (C:H₂O:O₂ = 1:0.25:y).

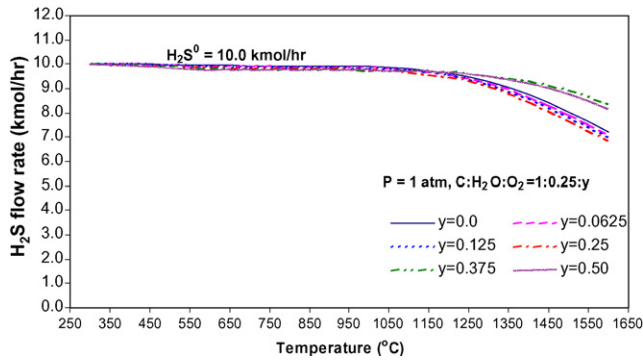


Fig. 10. Temperature dependence of H_2S flow rates at different oxygen inputs ($C:H_2O:O_2 = 1:0.25:y$).

0.50, the significant increases in CO output indicate a higher level of CO_2 generated. CO_2 outputs obviously increase to a significantly higher level when y is greater 0.50.

3.3. Equilibrium mole flow rates of hydrogen sulfide, carbonyl sulfide, sulfur disulfide and sulfur dimer during autothermal SRSQNG

Equilibrium outputs of H_2S at $x=0.25$, with varying levels of oxygen input are depicted in Fig. 10. The stability of H_2S during the course of autothermal SRSQNG is similar to that in SRSQNG shown in Fig. 3. H_2S is more stable at temperatures lower than $1000^\circ C$. The water input rate does not have significant effect on its stability. On the other hand, in a lower temperature range ($T < 1000^\circ C$), oxygen level does not have a significant effect on H_2S conversion, even at a higher level of $y (=0.5)$. Interestingly, when temperature is higher than $1300^\circ C$, the effect of oxygen on H_2S conversion increases within $y = 0.0-0.25$ range. However, H_2S output is stable when $y = 0.375$. There is only a slight decrease in H_2S concentration when $y = 0.50$. This observation is true for both $x = 0.0625$ and $x = 0.25$. With reference to Fig. 3 we observe that the oxygen effect on the H_2S conversion is similar to the effect of water input rate. This is due to the fact that oxygen reacts with hydrocarbons in SQNG to produce H_2O .

Unlike the effect of H_2O on COS output rates, increasing the oxygen inlet rate results in the higher CS_2 production rates shown in Fig. 11. The effect is more significant at a low water

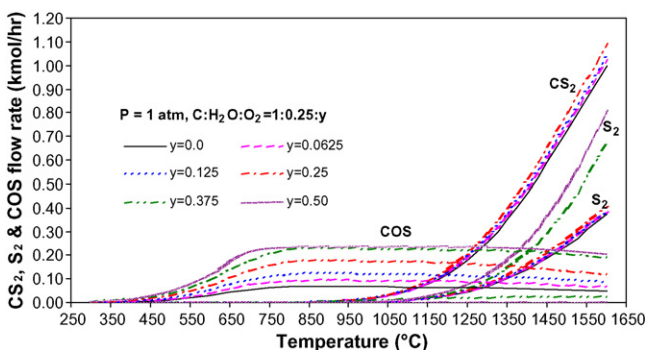


Fig. 11. Temperature dependence of CS_2 , COS and S_2 flow rates at various oxygen inputs ($C:H_2O:O_2 = 1:0.25:y$).

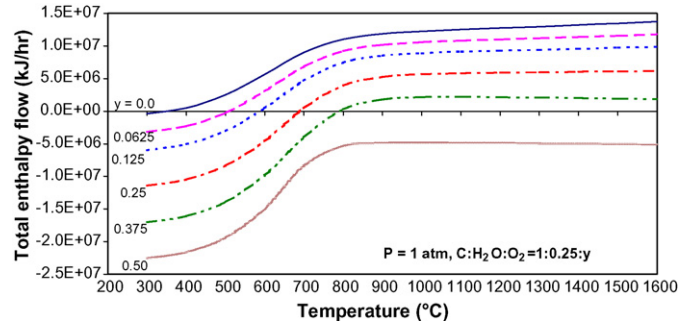


Fig. 12. Temperature dependence of total enthalpy at different oxygen inputs ($C:H_2O:O_2 = 1:0.25:y$).

input rate. However, the effects of oxygen on output rates of CS_2 and S_2 are similar to the effects of water (Fig. 4). When temperature is greater than $1100^\circ C$, the CS_2 production rate increases as y increases. However, when y increases up to 0.375, the CS_2 production rate approaches zero. The dependence of S_2 output rates on oxygen does not change significantly when y is less than 0.375. Starting at $y = 0.375$, S_2 outlet rates change significantly with y . However, it should be noted that the S_2 products are at a very low level, with concentrations in the ppm range. In the temperature range of $700-1000^\circ C$ COS is a major co-product, while concentrations of CS_2 and S_2 approach zero.

3.4. Heat requirements for autothermal SRSQNG processes

Heat requirements for the autothermal SRSQNG process are depicted in Fig. 12 for $x=0.25$. With increases in the oxygen inlet flow rate the total thermal energy requirement decreases significantly. Comparing two oxygen inlet levels ($x = 0.0625$ and $x = 0.25$) it is found that with increased water input to the system, greater oxygen inputs are required to reach a zero energy requirement condition. When $x=0.25$, the zero energy input temperature is about $800^\circ C$ with $y = 0.375$. But when $x = 0.0625$ and with the same oxygen input rate, the SRSQNG is an exothermal process, indicating that more hydrocarbons in SQNG are burned to recover only heating value. This results in a waste of valuable hydrocarbons which could be H_2 sources.

4. Flowsheet development

It has been reported that approximately one-third of U.S. natural gas resources are unusable SQNGs. H_2 production from SQNGs remains a major challenge due to substantial levels of embedded H_2S . Because of high costs associated with current technologies designed to deal only with high quality natural gases, SQNGs cannot presently be utilized for the production of H_2 and they must remain in the ground. As fossil fuel prices escalate SQNGs are becoming increasingly attractive as valuable potential resources for the production of H_2 . As compared to H_2 production from water, coal or biomass, the prospect of H_2 production from SQNGs could have many advantages in terms of efficiency and high H_2 yield.

As has been discussed in detail, H_2S in SQNG can be treated as an inert gas during the pyrolysis of SQNG, SRSQNG

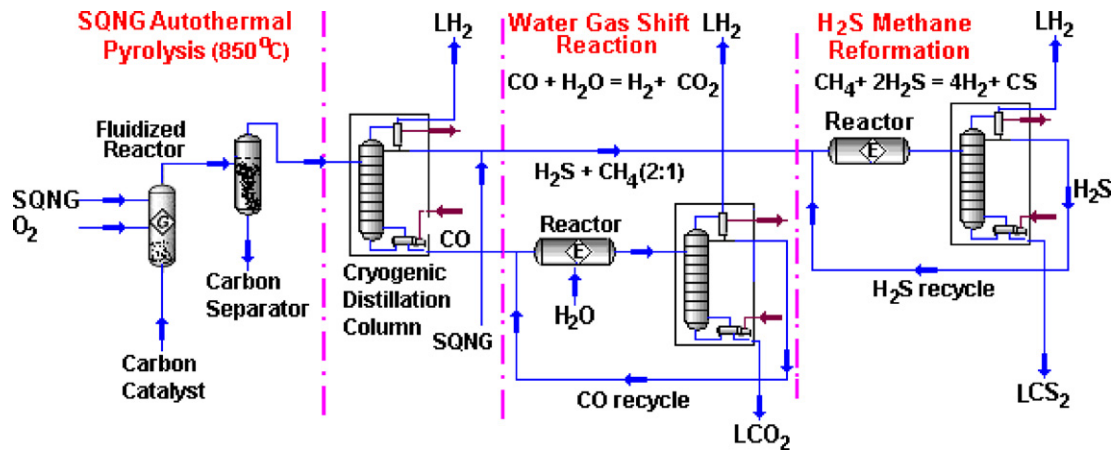


Fig. 13. Schematic diagram of a two-step H₂ production from SQNGs.

and autothermal processes when temperatures are lower than 1000 °C. Therefore, thermodynamically there is no need to separate H₂S from hydrocarbons prior to SQNG processing if no catalyst deactivation issue is involved. Using carbon-based catalysts and a fluidized reactor, we propose the following two-step process (Fig. 13) for H₂ production from SQNG. It should be pointed out that detailed flowsheet development is beyond the scope of this paper. Fig. 13 demonstrates only one approach for the production of liquid hydrogen (LH₂) for space applications. Similar processes based on different separation technologies, such as pressure swing adsorption and membrane separation, can be developed based on this concept.

4.1. Hydrocarbon processing (including SQNG pyrolysis, SRSQNG, autothermal pyrolysis or autothermal SRSQNG)

The mixture of SQNG and oxygen is inlet into a fluidized reactor which contains a carbon-based catalyst. The temperature of the autothermal process can be selected based on the previous thermodynamic calculations. A typical temperature of 850 °C is selected in this simplified flow diagram. (Fig. 13) After the SQNG autothermal process and separating the catalyst, H₂ and CO are cryogenically separated from the mixture of H₂S and unreacted CH₄. CO is then shifted into H₂ and CO₂ through a water gas shift reactor. By introducing a small amount of SQNG into the mixture of CH₄ + H₂S, the ratio of H₂S/CH₄ (or H₂S/C) can be adjusted to 2:1 in accordance with the stoichiometric coefficient of reaction: CH₄ + 2H₂S → 4H₂ + CS₂.

4.2. H₂S reforming of CH₄ (HSRM) [3] to efficiently produce H₂ and CS₂

In the HSRM process, an extra amount of H₂S is needed to serve two purposes: (1) as a working fluid and (2) to prevent carbon lay down from occurring. After reforming, H₂ and CS₂ are separated cryogenically and the extra H₂S keeps recycling in the system without being consumed. The selection of reforming conditions is based on the pinch points at which carbon lay down will not occur. Note that this conceptual design is a purely thermal process and would be highly efficient because no H₂S

separation is involved. The process combines H₂ production, purification and liquefaction into one process. The operations of cryogenic separation are employed to separate H₂, CO₂ and CS₂ from the gaseous mixtures and at the same time to liquefy them for the production of high purity LH₂, liquid CO₂ (LCO₂) and liquid CS₂ (LCS₂). As is widely known, LH₂ is in great demand for use in fueling space launches and also potentially for on board storage in vehicles. Detailed flowsheet development and analyses of LH₂ production from natural gas and from H₂S methane reforming can be found in Refs. [3,4].

5. Discussion of catalyst deactivation

As shown in Fig. 13, the innovative approach for H₂ production via SQNG proposed in this paper includes two fundamental steps: (1) H₂ production from CH₄ in SQNG in the presence of H₂S and (2) H₂ production via H₂S methane reforming. The second step has been carefully iterated in our previous paper [3]. It is therefore critical that the catalyst deactivation issue in the first step be solved in order to assemble a complete process. The challenge is to identify catalysts for hydrocarbon processing in the presence of H₂S. Conventional catalysts employed for SMR and/or CH₄ partial oxidation are Ni, Fe and Co metal-based catalysts. Some noble metal catalysts, such as Pt, Ag and Rh, are occasionally reported to reduce catalyst deactivation due to their higher tolerance for coking. A detailed discussion of the sulfur poisoning of metals can be found in reference [5]. The main mechanism of the deactivation of metal catalysts (M) used for SMR is the chemisorption of H₂S onto the metal surfaces forming surface metal sulfide according to the following reaction [5]:



The adsorption free energy, ΔG° (kJ mol⁻¹), can be written as:

$$\Delta G^\circ = RT \ln \left(\frac{P_{H_2S}}{P_{H_2}} \right) \quad (5)$$

In the typical range of reforming temperatures, namely 750–1000 °C, the free energy of formation for given metal sul-

fides is highly negative, indicating that the formation of these sulfides is thermodynamically favorable. The ratios of partial pressures of H_2S to H_2 (P_{H_2S}/P_{H_2}) calculated from the formation of free energy for metal sulfides are in the ppm range, suggesting a very low H_2S tolerant concentration is allowed in SRM to avoid H_2S chemisorption. Elevating reaction temperatures and/or H_2 concentration could increase the H_2S tolerance of metal catalysts, but such increase does not go beyond the ppm range. In addition to thermodynamic considerations, the formation of metal sulfides occurs as a rapid reaction. This can result in the deactivation of metal-based catalysts before a system temperature reaches reaction temperature range. Therefore, both thermodynamically and kinetically, metal-based catalysts are very sensitive to H_2S concentration and their tolerance to H_2S cannot be greater than ppm range.

With respect to Florida SQNG containing 10% H_2S , any metal catalysts mentioned above would be unsuitable. Fortunately, thermodynamic analyses in this paper (Parts I and II) reveal that elemental carbon is inert to H_2S at temperatures less than 1500 °C. This can be seen from the extremely low equilibrium composition of sulfur compounds CS_2 and COS . Accordingly, carbon-based catalysts can be used in the thermal pyrolysis and/or reforming of CH_4 to produce C and H_2 in the presence of H_2S . Muradov et al. [6–10] has applied carbon-based catalysts in CH_4 pyrolysis for the production of H_2 and carbon whiskers with reduced CO_2 emissions. However, as is widely known, the deactivation of carbon catalysts due to coking is another major difficulty. The following are two possible approaches for increasing carbon catalyst lifetimes.

5.1. In a fixed bed reactor

Since deactivation results from carbon deposition, the reduction of coking will prolong catalyst lifetime. This can be accomplished by introducing oxygen to the CH_4 pyrolytic process. The results have readily shown that the lifetime of the carbon catalyst has been enhanced in the autothermal pyrolytic process rather than in the pure CH_4 pyrolysis. The other issue is that in the presence of H_2S , carbon from CH_4 pyrolysis may be contaminated by sulfur deposition, reducing the quality and value of the carbon product. Reviewing the thermodynamic results presented in this paper we can observe two important facts: (1) the volume of sulfur generated as a byproduct of SQNG pyrolysis is very low (ppm range) and (2) at temperatures between 750 and 1000 °C sulfur exists in a gaseous state. Therefore, the low concentration gaseous sulfur should not cause the contamination of the carbon product.

5.2. In a fluidized bed reactor

A fluidized bed reactor could be utilized to resolve the carbon catalyst deactivation issue because carbon catalyst can be regenerated and/or recycled outside the fluidized reactor. During the processing of SQNG, carbon produced is deposited on the catalyst surface and can be separated from the gaseous stream as

a product. With fresh carbon catalyst being continuously added to the system the deactivation deadlock is automatically solved. However, an important issue which needs to be addressed is the relative values of the carbon catalyst and the carbon products generated during the process. If the latter value is greater than the former, then there would be no cost issues. However, if the carbon catalyst is more expensive than the carbon produced, then additional measures must be taken to prolong catalyst lifetime. These could include increasing oxygen and/or water flow to reduce carbon deposition, catalyst regeneration, catalyst pre-treatment, etc.

6. Conclusions

SQNG could become an important resource for hydrogen production. Steam reforming and autothermal steam reforming can be utilized for hydrogen production via SQNG. The thermodynamic analyses reported in this paper reveal that, within the SRSQNG and autothermal SRSQNG temperature range of 700–1000 °C, H_2S in SQNG is highly stable due to the presence of a high concentration of hydrogen produced from hydrocarbon processing. Therefore, H_2S can be treated as an inert gas during steam methane reforming at temperatures lower than 1000 °C. The only detectable product resulting from the H_2S conversion is carbonyl sulfide, which is in ppm range. The thermodynamic analyses reveal a possibility of treating SQNG in two steps: (I) hydrocarbon processing and (II) H_2S methane reforming, without requiring prior H_2S separation. An autothermal process could also be used for hydrogen production through SQNG with a reduced heat energy requirement.

Acknowledgment

The authors are grateful for the financial support of the NASA-GRC Grant NAG3-2751 hydrogen project.

References

- [1] C., Huang, A. T-Raissi, Thermodynamic analyses of hydrogen production from sub-quality natural gas (part I): pyrolysis and autothermal pyrolysis, J. Power Sources, Special Issue, ACS Washington.
- [2] C. Huang, A. T-Raissi, Analyses of hydrogen production from sub-quality natural gas (I): SQNG thermal decomposition and autothermal processes, Preprints of Symposia—American Chemical Society, vol. 50, no. 2, Division of Fuel Chemistry, 2005, pp. 470–471.
- [3] C. Huang, A. T-Raissi, Liquid hydrogen production via hydrogen sulfide methane reformation, Preprints of Symposia—American Chemical Society, vol. 49, no. 2, Division of Fuel Chemistry, 2004.
- [4] C. Huang, A. T-Raissi, Liquid hydrogen production via methane and landfill gas, in: 15th International Hydrogen Energy Conference, Yokohama, Japan, 2004.
- [5] C.H. BartholSSSomew, P.K. Agrawal, J.R. Katzer, Sulfur poisoning of metals, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.), Advances in Catalysis, vol. 31, 1982, pp. 135–235.
- [6] N. Muradov, F. Smith, A. T-Raissi, Catalytic activity of carbons for methane decomposition reaction, Catal. Today 102–103 (2005) 225–233.

- [7] N. Muradov, A. Schwitter, Formation of conical carbon structures on vapor-grown carbon filaments, *Nano Lett.* 2 (6) (2002) 673–676.
- [8] Muradov, Z. Nazim, CO₂-free production of hydrogen by catalytic pyrolysis of hydrocarbon fuel, *Energy Fuels* 12 (1) (1998) 41–48.
- [9] N.Z. Muradov, T.N. Veziroglu, From hydrocarbon to hydrogen-carbon to hydrogen economy, *Int. J. Hydrogen Energy* 30 (3) (2005) 225–237.
- [10] N.Z. Muradov, How to produce hydrogen from fossil fuels without carbon dioxide emission, *Int. J. Hydrogen Energy* 18 (3) (1993) 211–215.