

Thermodynamic analyses of hydrogen production from sub-quality natural gas

Part I: Pyrolysis and autothermal pyrolysis

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Abstract

Sub-quality natural gas (SQNG) is defined as natural gas whose composition exceeds pipeline specifications of nitrogen, carbon dioxide (CO₂) and/or hydrogen sulfide (H₂S). Approximately one-third of the U.S. natural gas resource is sub-quality gas [1]. Due to the high cost of removing H₂S from hydrocarbons using current processing technologies, SQNG wells are often capped and the gas remains in the ground. We propose and analyze a two-step hydrogen production scheme using SQNG as feedstock. The first step of the process involves hydrocarbon processing (via steam–methane reformation, autothermal steam–methane reformation, pyrolysis and autothermal pyrolysis) in the presence of H₂S. Our analyses reveal that H₂S existing in SQNG is stable and can be considered as an inert gas. No sulfur dioxide (SO₂) and/or sulfur trioxide (SO₃) is formed from the introduction of oxygen to SQNG. In the second step, after the separation of hydrogen from the main stream, un-reacted H₂S is used to reform the remaining methane, generating more hydrogen and carbon disulfide (CS₂). Thermodynamic analyses on SQNG feedstock containing up to 10% (v/v) H₂S have shown that no H₂S separation is required in this process. The Part I of this paper includes only thermodynamic analyses for SQNG pyrolysis and autothermal pyrolysis.

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1. Introduction

As the prices of fossil fuel increase, abundant SQNG resources become important alternatives to replace increasingly exhausted reserves of high quality natural gases for the production of hydrogen. Since SQNGs contain highly concentrated hydrocarbons compared to other sources (such as landfill gas and biomass), SQNGs are valuable resources. Additionally, H₂S in SQNGs is a highly concentrated sulfur source that can be utilized through H₂S methane reformation to produce H₂ and CS₂, a desirable raw chemical for the synthesis of sulfuric acid. Representative ranges of U.S. gas compositions and typical pipeline specifications are listed in Table 1 [2,3].

To achieve the required specifications for pipeline transmission of natural gas three basic issues need to be considered. The

first issue is the removal of impurities. The greatest concern for the quality of natural gas is the concentration level of any of the following impurities: H₂S, CO₂, H₂O and/or N₂. Since the latter three components only affect the heating value of the natural gas, they do not have a significant impact if the natural gas is to be used for the production of H₂. Water is required for steam methane reforming (SMR) while CO₂ and N₂ can be removed through a pressure swing adsorption process. However, H₂S in natural gas not only causes severe corrosion to pipelines, but it also deactivates catalysts during SMR. In addition to the corrosive and catalyst deactivation effects, it is well known that H₂S is an extremely toxic air pollutant. The second issue is the loss of CH₄ during the impurity removal processes. It is acceptable [2] if the loss is less than 3%, while losses over 10% are unacceptable. With the offset of other advantages, losses between 3% and 10% can be acceptable. The third issue is the final disposition of impurities removed from the original natural gas. It is well known that CO₂ is a greenhouse gas and needs to be sequestered. Removed H₂S also requires treatment to reduce its

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Table 1
Typical natural gas pipeline specification and composition ranges [2,3]

Component	Typical pipeline specification	Typical composition range	Percentage of resources
Hydrogen sulfide, H ₂ S	<4 ppm	<4 ppm	76
		4–1000 ppm	11
		1000–10000 ppm	4
Carbon dioxide, CO ₂	80–140 ppm	>10000 ppm	8
		<1%	72
		3–10%	3
Water, H ₂ O	80–1400 ppm	800–1200 ppm	
Nitrogen [3], N ₂	1.10%	0–30%	

environmental impact. Fortunately it is a useful resource for the production of hydrogen and sulfur.

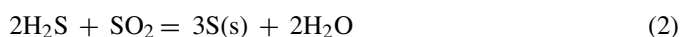
H₂S separation from CH₄ and its subsequent treatment constitute the main costs of SQNG utilization. When H₂S concentration in natural gas is higher than about 1.0% the high separation cost makes the SQNG economically unfeasible as an energy production source. As Lokhandwala et al. [1] pointed out, the best treatment for natural gas right now is no treatment, which means that millions of tons of SQNGs must remain underground and they require occasional monitoring of their release of H₂S. With today's increasing demand for domestic energy sources, thoughtful analysis and evaluation must be given to these potentially valuable hydrogen resources. The objective of this paper is to analyze possibilities for efficient production of H₂, sulfur and/or CS₂ from SQNGs without requiring an H₂S separation process. The catalyst deactivation issue and flowsheet development will be discussed in detail in the Part II of this paper.

2. Review of technologies

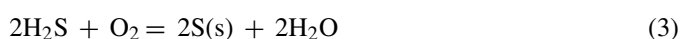
Several technologies are potentially applicable for the separation of H₂S from methane and hydrocarbons in SQNGs. After separation, methane can be reformed with water to produce H₂, and H₂S can undergo decomposition to produce H₂ and elemental sulfur.

2.1. Amine absorption and Claus plant

This technology uses amine absorption to separate H₂S from hydrocarbons. The separated H₂S then undergoes a Claus process in which a portion of H₂S is oxidized to produce SO₂, and the latter is then recombined with the main H₂S to produce elemental sulfur and water vapor according to:



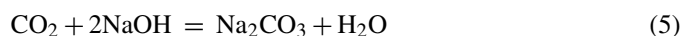
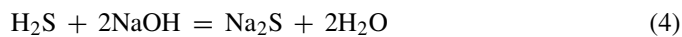
Thus the overall reaction can be written as:



One of the technological merits of this approach is that both amine absorption and Claus plants are commercialized and suitable for large-scale SQNG treatment. However, in this process the H₂ in H₂S is wasted as water vapor. Furthermore, since Claus units cannot convert 100% of the H₂S into sulfur, tail gas cleanup units are needed to reduce the environmental issues related to SO₂ discharge. In addition to the Claus process, some innovative processes for utilizing H₂S both as H₂ and sulfur sources have been widely explored for decades. The typical approaches include thermochemical methods, electrochemical methods, photochemical methods and plasma methods. A detailed review and comparison of these methods is given by Zaman and Chakma [4].

2.2. Alkaline absorption + electrolysis (or photolysis)

With the exception of amine absorption, H₂S and CO₂ in SQNG can be most readily absorbed by an alkaline solution through the following reactions:

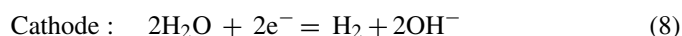
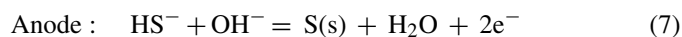


CH₄ and other hydrocarbons in SQNG will not be absorbed and thus be separated. This absorption process is far less complicated than amine absorption and there is no amine final treatment needed. The remaining problem is to convert sodium sulfide (Na₂S) into H₂ and sulfur and to re-circulate the alkaline solution (NaOH). Typically, there are two technologies which can be utilized in the production of hydrogen from Na₂S: electrochemical methods and photochemical methods.

Bisulfide ions (HS⁻) are formed when H₂S is dissolved in an alkaline solution according to:



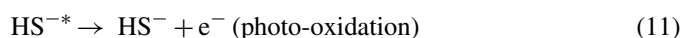
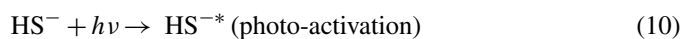
During the electrolytic process sulfur is generated at the anode and hydrogen is evolved at the cathode in the following electrochemical reactions [4]:



The overall reaction for reactions (6)–(8) is:



No alkali is consumed during this process, forming a closed-cycle. A similar process can be applied to the UV light photolytic decomposition of sodium sulfide for the production of hydrogen and sulfur [6]. It has been found that a Na₂S aqueous solution can be photolytically dissociated into hydrogen and sodium disulfide (Na₂S₂) according to the following [6,7]:





The overall reaction of reactions (10)–(13) is:



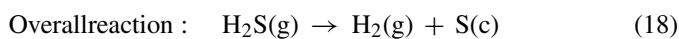
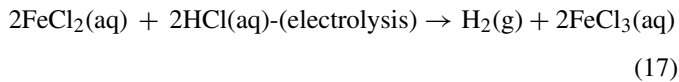
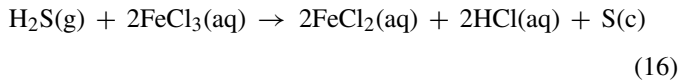
Disulfide ions can further react with H_2S to produce bisulfide ions and solid sulfur, forming the following closed cycle:



No photocatalysts are needed in this process, avoiding deactivation of catalysts or passivation of electrodes for electrochemical processes. One important characteristic of the photolytic process is that [6,7] the concentration of sodium carbonate dissolved in solution (reaction (5)) does not affect the hydrogen evolution rate. Clearly, this approach can be applied to remove H_2S from SQNG and then utilize it to produce hydrogen and sulfur. The disadvantage of the approach is that electrical energy must be converted into photonic energy, causing energy loss.

2.3. Fe–Cl hybrid process (FeCl_3 + electrolysis)

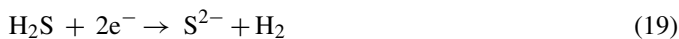
Mizuta et al. [4,8–11] developed a hybrid process based on iron chloride for the production of hydrogen and sulfur from H_2S . The process consists of a H_2S absorption step and an electrolysis step according to the following reactions:



It is reported that the process can approximate 100% H_2S absorption at 343 K. The electrolysis requires a voltage of 0.7 V and 100 mA cm^{-2} current density. The feed gas used was a mixture of 30% H_2S and 70% argon.

2.4. High temperature electrolysis

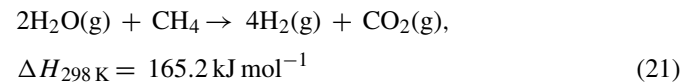
This process does not require a separation step. SQNGs can be fed into a high temperature cathode where H_2S is directly converted into hydrogen and sulfur while being separated from methane and hydrocarbons. The produced hydrogen enters the process stream while sulfur is condensed and collected as a product [2,4–6]. The electrochemical reaction takes place as:



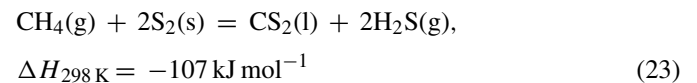
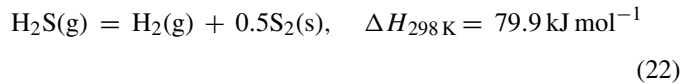
Up to 80.7% of the H_2S can be removed from an input 2000 ppm H_2S . The process can also remove carbon dioxide from natural gas.

2.5. Hydrogen sulfide methane reformation [12,13]

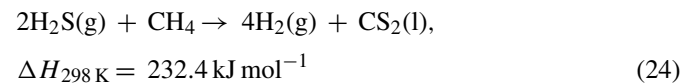
Similar to SMR:



H_2S can reform with methane to produce hydrogen and CS_2 . The reformation consists of two steps:



The overall reaction can be written as:



The advantages of this process are obvious. Firstly, no separation of H_2S from methane is needed. Secondly, unlike elemental sulfur, the CS_2 produced from the reformation has broad applications. It can be used for the production of sulfuric acid and the manufacture of xanthate. Thirdly, the process does not produce CO_2 as does SMR, thus greatly reducing greenhouse emission. Fourthly, since the reformation is a highly endothermic process, it can be used to efficiently absorb heat from a high temperature heat source and is potentially applicable for absorbing concentrated solar energy.

It is noteworthy that during H_2S methane reformation, methane can decompose to form carbon deposits as:



Carbon coking can cause the deactivation of reforming catalysts. So conditions chosen for reaction (24) must guarantee that no carbon lay-down occurs during the process. The thermodynamic analysis of reaction (25) has revealed [12,13] that there exist pinch points at which no methane decomposes when the ratio of H_2S to CH_4 ($\text{H}_2\text{S}:\text{CH}_4$) is greater than 4. The pinch point temperature decreases as the ratio increases. Based on the stoichiometric coefficient of reaction (24), H_2S methane reformation requires 2:1 for the ratio of $\text{H}_2\text{S}:\text{CH}_4$, which corresponds to 67% H_2S in SQNG. Therefore, this reformation can only apply to those very soured SQNGs with a H_2S concentration greater than 67%. For most SQNGs with a few percent of H_2S , the reformation requires extra H_2S input in order to meet the stoichiometric requirement. In summary, the applicable technologies discussed above are listed in Table 2.

As mentioned above, the objective of this research was to explore possibilities via thermodynamic analyses for efficiently producing hydrogen, sulfur and/or CS_2 from SQNG. A typical SQNG composition of 10% H_2S (the Blackjack Creek SQNG field in the Florida panhandle area (Table 3)) was selected for the

Table 2
Comparison of possible technologies for hydrogen sulfide separation and treatment in natural gases

Technology	Advantage	Disadvantage	Reference
Amine absorption + Claus plant	Commercialized	No H ₂ produced. Amine regeneration needed. Limited H ₂ S absorption. Tail gas treatment	[5]
Alkaline absorption + electrolysis	Fast and selective absorption. High H ₂ S concentration absorption. High efficiency H ₂ and S production	Anode passivation	[4,6]
Alkaline absorption + photolysis	Fast and selective absorption. High H ₂ S concentration absorption. High efficiency H ₂ and S production	Low quantum efficiency	[6,7]
Fe–Cl hybrid process. FeCl ₃ absorption + electrolysis	Fast and selective absorption. High H ₂ S concentration absorption. High efficiency H ₂ and S production	Highly acidic process	[4,8–11]
H ₂ S CH ₄ reforming 2H ₂ S + CH ₄ = 4H ₂ + CS ₂	No H ₂ S separation needed. Co-producing CS ₂ . Pure thermal process	High temperature required. High H ₂ S to CH ₄ ratio required. Only applied H ₂ S >80% natural gas	[12,13]

Table 3
Gas compositions of Florida Blackjack Creek SQNG resource^a

Composition mol%	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₆ H ₁₄	H ₂ S	CO ₂	N ₂	He	Other
	62.10	11.70	3.40	2.30	0.80	0.20	10.00	2.40	6.90	0.04	0.10

^a Total carbon concentration is 110 mol%. This is calculated as the sum of carbon moles in hydrocarbons. For example, C₂H₆ concentration is 11.7 mol%. The carbon moles in C₂H₆ are 2, so the carbon concentration is calculated as 23.4%.

thermodynamic calculation. The thermodynamic analyses were performed using a Gibbs reactor operation in the AspenPlusTM chemical process simulator. Concentrations of SQNG (Table 3) were used as inlet concentrations to the Gibbs reactor and outlet equilibrium concentrations were determined by minimization of Gibbs free energy from the reactor under isothermal conditions.

3. Thermal decomposition of SQNG

H₂ production through natural gas pyrolysis or autothermal process has been extensively reported. However, H₂ production via SQNG pyrolysis in the presence of H₂S is rare in literature citations. One major reason for this is that H₂S component is harmful to the methane pyrolysis catalysts. Another important consideration is the final disposition of the H₂S that must be removed either from its source SQNG or from the product mixture. The commonly accepted approach is to remove it prior to the natural gas pyrolytic process. This approach is costly and requires follow up treatment. An unanswered question is whether or not hydrocarbons can be thermochemically decomposed to produce hydrogen in the presence of H₂S. If, in the methane pyrolysis temperature range, H₂S is stable, the H₂ produced can be easily separated from the main stream with many readily available technologies, while the remaining H₂S and un-decomposed CH₄ can reform to further produce H₂ and CS₂. This approach greatly reduces the H₂S separation costs. Furthermore, as reviewed above, H₂S methane reformation is a less costly process than either electrolysis or photolysis for the utilization of H₂S. In addition to H₂ production, the reformation process can produce a higher value product, CS₂. Unlike metal catalysts, carbon based catalysts will not be affected by the presence of H₂S, and therefore can be used in the pyrolysis of SQNG.

We take the Blackjack Creek SQNG source (Table 3) as a case study. The thermodynamic analysis is conducted based on an assumed isothermal process. In this calculation we also assume that the inlet component mole flow rates to a Gibbs reactor are equal to their mole fractions listed in Table 3. For example, the 62.10% of CH₄ mole concentration becomes the CH₄ initial flow rate of 62.1 kmol h⁻¹ as indicated in Fig. 1.

3.1. Equilibrium flow rates of methane, hydrogen and carbon

Fig. 1 shows the equilibrium flow rates of CH₄, H₂ and C at various pyrolytic temperatures. When the temperature is lower than 500 °C, hydrocarbons (C₂–C₆) are decomposed to produce CH₄ and H₂. CH₄ flow rate increases from the initial 62.1 to about 90 kmol h⁻¹ at 300 °C. With increasing temperature the CH₄ flow rate decreases. When the temperature exceeds 500 °C CH₄ is decomposed into C and H₂. When the temperature is

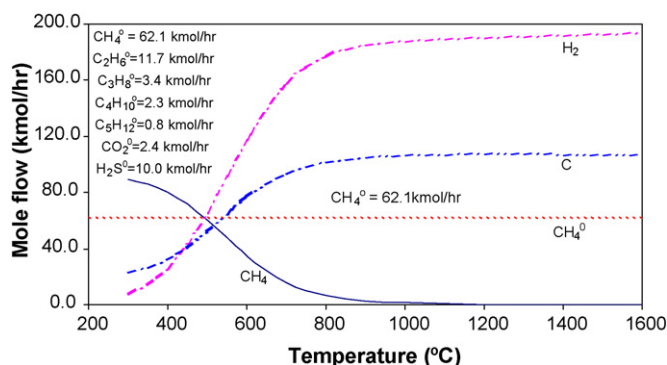


Fig. 1. Temperature dependence of CH₄, H₂ and C equilibrium flow rates for SQNG pyrolysis at P = 1.0 atm.

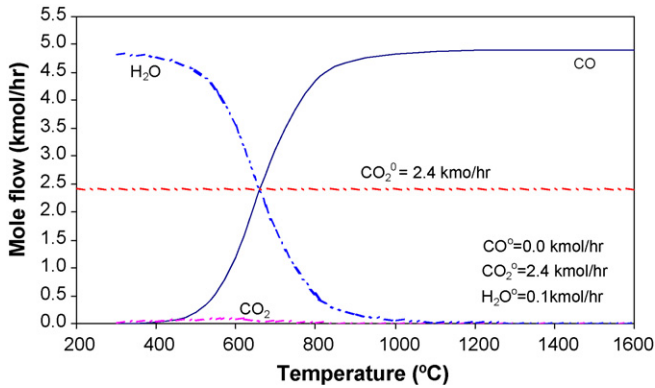
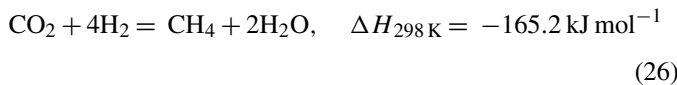


Fig. 2. Temperature dependence of H₂O, CO₂ and CO equilibrium flow rates for SQNG pyrolysis at $P = 1.0$ atm.

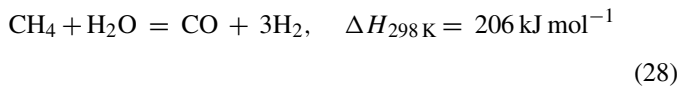
higher than 850 °C equilibrium flow rates of H₂ and C just slightly increase with temperature increases.

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

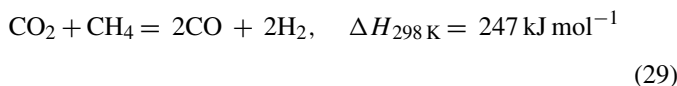
The removal of CO₂ from natural gas is one of the important steps in improving natural gas quality. The initial CO₂ and water flow rates are 2.4 and 0.1 kmol h⁻¹ while the CO flow rate is 0.0 kmol h⁻¹. Fig. 2 shows that the equilibrium flow rate of CO₂ is lower than 0.1 kmol h⁻¹ in the temperature range from 300 to 1600 °C. At a low temperature range (300–500 °C), the flow rate of CO is at a trace level, while the water flow rate is two times higher than the initial CO₂ flow rate. This result indicates that CO₂ is shifted to water and CH₄ according to reaction (26) while a water gas shift reaction is unlikely to occur (reaction (27)):



As a result, the abrupt increase in the methane flow rate shown in Fig. 1 is partially due to reaction (26). As the temperature increases, SMR occurs, to produce CO and hydrogen according to the following:



The overall reaction of reactions (26) and (28) can be written as:



Reaction (29) may indicate that CO₂ in SQNG can be reformed to produce CO and H₂.

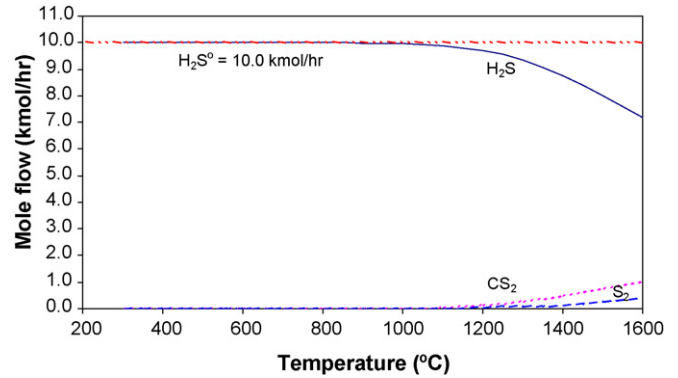


Fig. 3. Temperature dependence of H₂S, CS₂ and S₂ equilibrium flow rates for SQNG pyrolysis at $P = 1.0$ atm.

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

The behavior of H₂S during pyrolysis of hydrocarbons in SQNG is a major concern above all other issues. If H₂S is decomposed into H₂ and elemental sulfur, the pyrolysis is considered less practical because sulfur deposition will deactivate the catalysts of CH₄ decomposition. To evaluate H₂S decomposition, the best approach is to examine its stability during the pyrolytic process. The equilibrium flow rates of H₂S, CS₂ and sulfur dimer (S₂) are shown in Fig. 3. The initial mole fraction of H₂S is 10.0% corresponding to 10.0 kmol h⁻¹ inlet to a Gibbs reactor.

Two primary reactions for H₂S involved in the SQNG pyrolysis are H₂S decomposition (reaction (22)) and H₂S methane reforming (reaction (24)). The products of these two reactions are H₂S, S₂ and CS₂. Fig. 3 indicates that H₂S is stabilized when the temperature is lower than 1000 °C. Since the normal CH₄ pyrolysis temperature range is from 700 to 1000 °C, the stability of H₂S in this temperature range suggests that it can be treated as an inert gas that does not affect CH₄ pyrolysis. At a temperature greater than 1000 °C CH₄ reacts slightly with H₂S to produce low flow rates of CS₂. On the other hand, H₂S decomposition is unlikely to occur, even at very high temperatures, as indicated by the very low flow rate of S₂. At a temperature of 1000 °C, the S₂ flow rate is 0.00324 kmol h⁻¹ (lower than 0.3 ppm mole fraction in the outlet stream).

To illustrate the stability of pure H₂S, equilibrium calculations were conducted for H₂S at different pressures and temperatures. The results shown in Figs. 4 and 5 clearly indicate that pure H₂S is much easier to decompose than that in SQNG. The conversions of pure H₂S at temperature 1000 °C are 20% at pressure of 1 atm and 35% at 0.1 atm, respectively. Note that the H₂S conversion at pressure 0.1 atm is not shown in the figures. This conversion was calculated separately. The H₂S partial pressure in SQNG is 0.1 atm but the conversion is close to zero at the same temperature (Fig. 3). The result suggests that the stability of H₂S in SQNG pyrolysis is greatly enhanced by the presence of H₂ produced from hydrocarbon decomposition. Thus, H₂S in SQNG can be treated as an inert gas during the

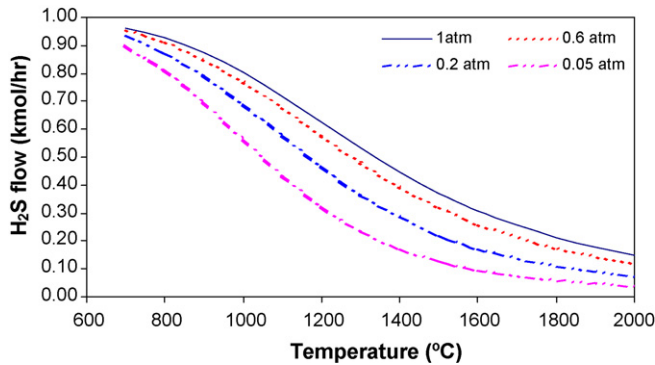


Fig. 4. Temperature dependence of equilibrium H_2S mole flow rates (1 kmol h^{-1} of initial inlet H_2S).

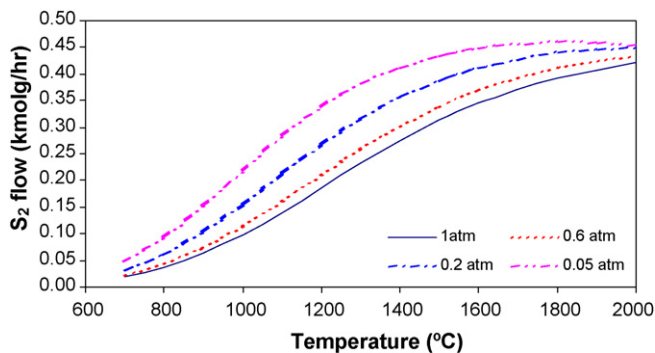


Fig. 5. Temperature dependence of equilibrium S_2 mole flow rates (1 kmol h^{-1} of initial inlet H_2S).

pyrolytic process and also if catalysts are used; no H_2S separation is required prior to pyrolysis. After pyrolysis, H_2S can be more easily separated from H_2 than from hydrocarbons prior to pyrolysis.

4. Autothermal decomposition of SQNG

SQNG pyrolysis is a highly endothermic process. In order to reduce the requirement for thermal energy for SQNG pyrolysis, hydrocarbons in SQNG can be partially oxidized to generate heat for the decomposition of the remaining hydrocarbons. If the thermal energy generated is equal to the required heat, no thermal energy input is needed. This process can be defined as SQNG autothermal decomposition. It differs from the autothermal decomposition of pure CH_4 because the presence of H_2S in SQNG may react with oxygen to produce environmentally harmful gases such as SO_2 or SO_3 . Therefore the key issue in autothermal decomposition of SQNG is whether the process generates SO_2 or SO_3 in the CH_4 pyrolysis temperature range. The oxygen source can be either pure oxygen or air. In this paper we used air as the oxygen source mixed with SQNG inlet into the Gibbs reactor under isothermal conditions and calculated equilibrium flow rates in the outlet stream. Inlet air flow rates to the Gibbs reactor are 0, 10, 20, 30, 40 and 80 kmol h^{-1} , corresponding to oxygen flow rates of 0, 2.1, 4.2, 6.3, 8.4 and 16.8 kmol h^{-1} , respectively.

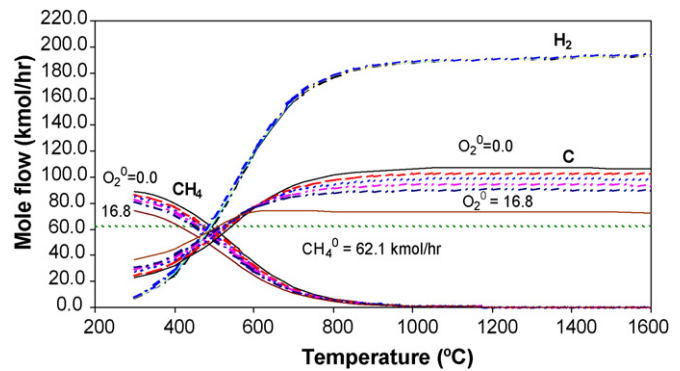


Fig. 6. Temperature dependence of equilibrium mole flow rates of CH_4 , H_2 and C in SQNG autothermal decomposition ($\text{O}_2 = 0.0, 2.1, 4.2, 6.3, 8.4$ and 16.8 kmol h^{-1}).

4.1. Equilibrium flow rates of methane, carbon and hydrogen during autothermal process

Fig. 6 depicts equilibrium flow rates of H_2 , C and CH_4 at various inlet oxygen levels. Firstly, similarly to the pyrolysis of SQNG, all other hydrocarbons are decomposed into H_2 , C and CH_4 within a temperature range of $300\text{--}500^\circ\text{C}$. CH_4 flow rates decrease with the increase of either temperature or oxygen flow rate. Interestingly, equilibrium H_2 output flow rates are independent of oxygen input within the range of $0\text{--}16.8 \text{ kmol h}^{-1}$. This may be due to the fact that a portion of H_2 production via CH_4 decomposition is reduced because of oxidation. However, water resulting from CH_4 oxidation can be reformed with the remaining CH_4 and/or C to produce more H_2 . Thus, the total H_2 produced does not decrease as the inlet oxygen flow rate increases. In comparison, carbon output can be separated into two temperature ranges: (1) $300\text{--}600^\circ\text{C}$ and $600\text{--}1600^\circ\text{C}$. Within the first range, equilibrium carbon output increases with the increase of the oxygen flow rate, suggesting that oxygen promotes the hydrocarbon decomposition process. In the second temperature range, carbon is partially oxidized into carbon oxides resulting in decreased carbon output.

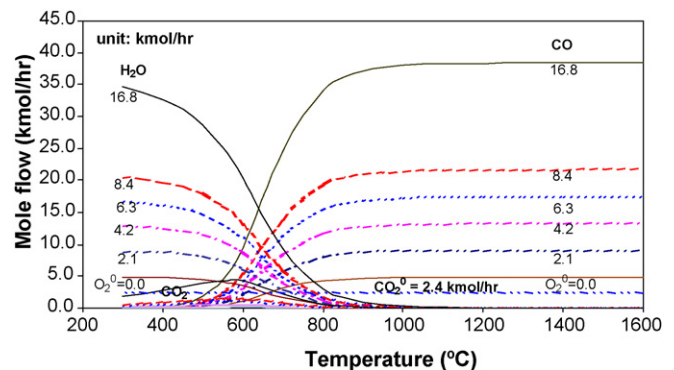


Fig. 7. Temperature dependence of equilibrium mole flow rates of CO_2 , CO and H_2O in SQNG autothermal process ($\text{O}_2 = 0.0, 2.1, 4.2, 6.3, 8.4$ and 6.8 kmol h^{-1}).

4.2. Equilibrium flow rates of carbon dioxide, carbon monoxide and water distribution during autothermal process

Fig. 7 demonstrates the equilibrium flow rates of CO₂, CO and H₂O during SQNG autothermal processes. In the lower temperature range (300–600 °C) the water output flow rate increases with the increase of the inlet oxygen flow rate. However, in the higher temperature range (600–1600 °C) increasing the oxygen flow rate increases CO output. CO produced must be shifted to produce H₂ and an equal molar amount of CO₂. Therefore, the increased oxygen level effectively increases CO₂ output. Thus, the autothermal process results in an increased greenhouse effect.

4.3. Equilibrium mole flow rates of hydrogen sulfide, sulfur disulfide and sulfur dimer during autothermal process

Equilibrium outputs of H₂S, CS₂ and S₂ at various oxygen inlet flow rates are depicted in Fig. 8. In the autothermal process of SQNG, oxygen level does not have a significant effect on the stability of H₂S. In the CH₄ decomposition temperature range (700–1000 °C), the H₂S stability data are of critical concern for the autothermal process. Equilibrium compositions for sulfur species, such as H₂S, CS₂, carbonyl sulfide (COS) and S₂ are listed in Table 4. The total outlet gas flow rates used for the calculation of concentrations include nitrogen from the air.

As indicated in Fig. 8 and Table 4, H₂S conversion in the temperature range of 700–1000 °C is at very low levels, with a maximum of 1.45% at a temperature of 1000 °C and an oxygen flow rate of 16.8 kmol h⁻¹. The conversion of H₂S increases only slightly with an increase of oxygen flow rate. The converted H₂S has four outlets: (1) decomposes into H₂ and S₂; (2) reacts with CH₄ to form CS₂; (3) combines with CO to produce COS; (4) oxidizes into SO₂. Fig. 8 indicates that H₂S decomposition is a weak function of the inlet oxygen flow rate, indicating that the oxygen inlet flow rate does not significantly affect either CS₂ or S₂ output flow rates. More detailed data are shown in Table 4. Since flow rates of SO₂ are in trace amounts during the autothermal processes, the effect of oxygen inlet flow rates on the production of SO₂ is negligible. Of the four components CS₂, S₂,

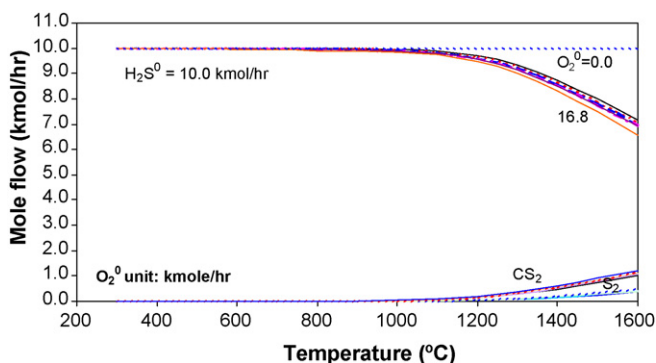


Fig. 8. Temperature dependence of equilibrium mole flow rates of H₂S, CS₂, S₂ in SQNG autothermal process (O₂ = 0.0, 2.1, 4.2, 6.3, 8.4 and 16.8 kmol h⁻¹).

Table 4

Sulfur species concentrations and H₂S conversions from temperature 700 to 1000 °C

Temperature (°C)	O ₂ (kmol h ⁻¹)					
	0.0	2.1	4.2	6.3	8.4	16.8
700						
H ₂ S (%)	0.00	0.18	0.27	0.35	0.43	0.76
CS ₂ (ppm)	0.88	0.88	0.87	0.87	0.86	0.85
S ₂ (ppm)	0.11	0.11	0.11	0.11	0.11	0.11
SO ₂ (ppm)	0.00	0.00	0.00	0.00	0.00	0.00
COS (ppm)	49.68	87.03	120.35	150.36	177.25	268.88
800						
H ₂ S (%)	0.00	0.24	0.34	0.44	0.53	0.93
CS ₂ (ppm)	0.88	4.21	4.77	4.74	4.72	4.66
S ₂ (ppm)	0.11	0.63	0.71	0.71	0.71	0.70
SO ₂ (ppm)	0.00	0.00	0.00	0.00	0.00	0.00
COS (ppm)	49.68	86.27	135.84	169.67	200.23	304.38
900						
H ₂ S (%)	0.11	0.33	0.43	0.54	0.64	1.06
CS ₂ (ppm)	21.81	21.66	21.58	21.50	4.72	21.17
S ₂ (ppm)	3.72	3.69	3.68	3.67	3.65	3.61
SO ₂ (ppm)	0.00	0.00	0.00	0.00	0.00	0.00
COS (ppm)	55.74	97.73	135.27	169.02	199.52	303.57
1000						
H ₂ S (%)	0.40	0.64	0.76	0.87	0.99	1.45
CS ₂ (ppm)	79.70	79.23	78.95	78.69	78.43	77.52
S ₂ (ppm)	15.36	15.27	15.21	15.16	15.11	14.94
SO ₂ (ppm)	0.00	0.00	0.00	0.00	0.00	0.00
COS (ppm)	54.56	95.69	135.01	165.54	195.42	297.37

SO₂ and COS, COS has the highest concentrations (50–300 ppm range). The concentration increases with the increase of the oxygen inlet flow rate. However, it is a weak function of temperature. COS is formed according to the following reaction:



The boiling temperature of carbonyl sulfide is –58 °C and it exists in a gaseous state.

4.4. Thermal energy calculation for autothermal process

Heat requirements are calculated as the differences of the total enthalpies in output and inlet streams of the Gibbs reactor during the SQNG autothermal process. These are given by the AspenPlusTM simulator and the results are depicted in Fig. 9. With increase in the oxygen inlet flow rate the total input heat requirement decreases significantly. The zero energy temperatures are defined as the enthalpy curves intersect the zero enthalpy flow line. Fig. 10 reveals a linear relationship between the zero heat input temperature and the oxygen flow rates:

$$T_{\Delta H=0} = 12.05 \times \text{O}_2 \text{ flow rate} + 440 \text{ (}^\circ\text{C)} \quad (31)$$

As discussed above, autothermal processes require reduced or zero energy input for the pyrolysis of SQNG. However, the input of oxygen produces a higher concentration of CO₂. This is a major disadvantage of the process. In order that the process can be operated in an optimal condition, the oxygen inlet flow rate should be established based on several parameters: minimum

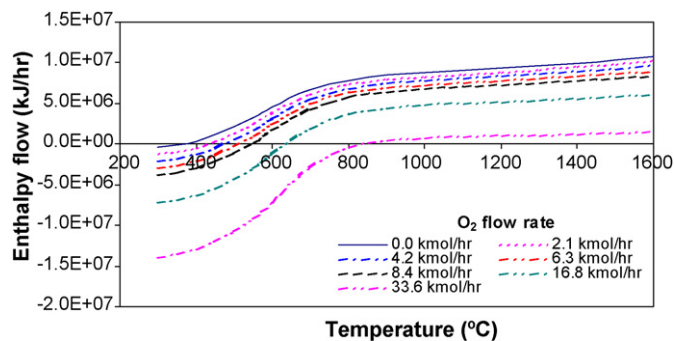


Fig. 9. Heat requirements in SQNG autothermal process at different oxygen levels ($O_2 = 0.0, 2.1, 4.2, 6.3, 8.4, 16.8$ and 33.6 kmol h^{-1}).

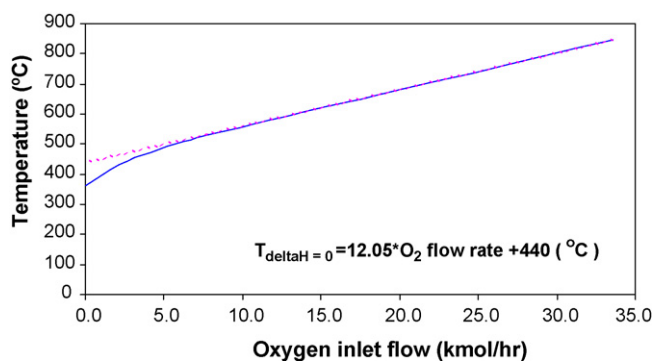


Fig. 10. Zero thermal energy requirement temperature vs. oxygen input flow rate.

heat input, minimum carbon dioxide output and maximum H_2 output.

5. Conclusions

SQNG can be an important H_2 source. Due to interference between the decomposition of H_2S and CH_4 , current technologies cannot be applied economically either for the production of H_2 or for pipeline natural gas production from SQNG. The thermodynamic analyses of SQNG pyrolysis and autothermal pyrolysis reveal for the first time that, within the CH_4 pyrolysis temperature range of $700\text{--}1000^\circ\text{C}$, H_2S in SQNG is highly stabilized due to the presence of H_2 . Therefore, H_2S can be treated

as an inert gas within this temperature range. The only detectable product resulting from the H_2S conversion is COS, which is in the ppm range. The thermodynamic analyses indicate a possibility of treating SQNG in two steps: hydrocarbon pyrolysis and H_2S methane reformation, without requiring prior H_2S separation. An autothermal process can also be used for H_2 production through SQNG with a reduced heat energy requirement. The zero input heat requirements are a linear function of the input oxygen flow rate.

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