Abstract

When reforming natural gas to obtain hydrogen and synthesis gas, it is taken for granted that the feed gas has to be sour-free. This is based on the ground that catalysts used in the reforming process are susceptible to poisoning by sulfur compounds. Therefore, we are faced with the dilemma of the exhaustive desulfurization process of the sour gas in order to make it sweet. The other option is to use thermal reforming and avoid the catalytic route. In this paper, trends in the reforming technology of natural gas, in general, are reviewed first. Next, novel trends in reforming sour natural gas, in particular, are presented using high temperature heat (H.T.H.) approach. This method can be carried out using non-catalytic partial oxidation NCPO in a chamber combustion (CC) or rich combustion in porous media (CPM). Simulation results for NCPO, reported earlier by Abdel-Aal et al. [1,2] are re-examined on the ground that using CPM is a promising method to handle the reforming of sour natural gas through the proposed given process-scheme. The application of ultra-rich super-adiabatic partial oxidation in an inert porous medium for hydrogen generation is a novel method of research and technology. This is particularly true when dealing with sour natural gas resources. The present contribution focuses on this approach. The review helps to document the foundation on which the needed development can build. The proposed scheme avoids the problem of separation of acidic gases and aims instead, to direct chemical conversion. The partial combustion of sour natural gas will end up converting the sulfur element into sulfuric acid as a co-product along with synthesis gas and hydrogen as end products.

Key Words: Sour natural gas, Reforming, Hydrogen, Non-catalytic partial oxidation

1. Introduction

A viable question could be asked: What is the largest single source of industrial hydrogen in the world? The answer could be either water or methane gas (natural gas). This is simply a matter of economics. It requires more energy to dissociate the elements of hydrogen and oxygen from the water molecule than it does to combine methane with steam to form hydrogen and carbon dioxide.

Current technology for hydrogen production from natural gas is mature and practiced on a large scale for producing methanol (MeOH), ammonia (NH3) and others, for the petrochemical industry and other uses. The major part of the world's hydrogen production is accomplished by steam methane reforming (SMR). This is a catalytic process that requires S-free feed stock of natural gas.

Natural gas is usually considered sour if there are more than 5.7 milligrams of H2S per cubic meter of natural gas, (around 4 ppm by volume). Worldwide, increasing energy costs and growing demand for natural gas along with deep gas-drilling have driven the development of sour gas fields around the world. In addition, about forty percent of the world's natural gas reserves are in the form of sour gas where H2S and CO2 compositions exceed 10% by volume.[3].
(TPOX) offers several advantages, such as: absence of catalysts which eliminates the catalyst deactivation problems; no need for external heat sources and additional feeds like water; good process dynamic response; and applicability to almost all hydrocarbons.

The application of high temperature heat in reforming sour natural gas is pursued in this presentation.

The work reported earlier[1, 2] on NCPO, offers a promising technique to recover the hydrogen component lost in the H2S molecule. In addition, many of the technical and economic hurdles currently encountered in the production of synthesis gas from sour natural resources are eliminated. The partial combustion of sour natural gas will end up converting the sulfur element into sulfuric acid as a co-product along with synthesis gas and hydrogen as end products. In Fig.1, a comparison is presented between the current technology of making synthesis gas from sour natural gas and the proposed NCPO.

From another perspective, research in the area of reforming using rich combustion in porous media, PMC,(known as filtration combustion), could lead to valuable applications in handling sour natural gas.PMC shows superior advantages compared with free flame combustion due to the higher burning rates, the increased power dynamic range, the extension of the lean flammability limits, and the low emissions of pollutants. Work published, however, handled only the case of sweet natural gas.[8-18].

2. Overview of Reforming Operations

The manufacture of syngas by reforming natural gas can be done using different approaches from partial oxidation reforming to auto-thermal reforming systems; and from steam reforming to dry reforming processes. For all operations, the process uses an oxidizing agent that will convert methane hydrocarbon into carbon monoxide and producing hydrogen in variable ratios according to the types of oxidizing agents used.

A concise classification of the different reforming operations is illustrated first, as shown in Fig. 2. Next, a brief outline of the main features underlying a process is presented.

The main features of the reforming processes are highlighted next:

- Methane reforming operation is mainly based on steam reforming, auto-thermal (ATR) reforming or partial oxidation. Its main objective is to produce synthesis gas, in particular pure hydrogen gas from methane. For catalytic technology, there are two methane reformer options: steam methane reforming (SMR) and auto-thermal reforming (ATR).

- Reforming of natural gas is sometimes referred to as steam-methane reforming as natural gas is predominately composed of methane.

- Reforming uses a nickel-based catalyst to promote the reaction. It proceeds according to the following reactions:

\[ \text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO} \]  
**Main Reaction** (1)

\[ \text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2 \]  
**Water-shift reaction** (2)

The overall reaction is described as endothermic

- Design parameters are: operating pressure, steam to carbon ratio in the feed, composition of the natural gas, the method of supplying the heat of reaction, and amount of carbon dioxide recycle

- Carbon dioxide recycle may be used to lower the ratio of H2/CO in the synthesis gas, by influencing the equilibrium in the reverse direction in the second reaction.

- Auto-thermal reforming (ATR) uses oxygen and carbon dioxide or steam in a reaction with methane to form syngas. It is a combination of non-catalytic partial oxidation and adiabatic steam reforming. The main difference between SMR and ATR is that SMR uses no oxygen. An ATR reactor contains a combustion zone at the top and a catalyst filled bed at the bottom.

- Partial oxidation (POX) is used to generate synthesis gas. POX is a non-catalytic process in which the feed is partially combusted with air, oxygen, or enriched air to make synthesis gas. In partial oxidation, the methane and other hydrocarbons in natural gas react with a limited amount of oxygen (typically from air) that is not enough to completely oxidize the hydrocarbons to carbon dioxide and water. Two alternatives exist:

  (a) The non-catalytic route known as thermal partial oxidation (TPOX)

  (b) The catalytic route known as CPOX

Oxidation reaction is represented as given next:

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 (+ \text{heat}) \]  
**Oxidation reaction** (3)

- Non-Catalytic Partial Oxidation of Sour Natural gas (NCPO): It involves the simultaneous partial combustion of methane along with the complete combustion of H2S. Reactions are represented by equations (4) and (5):

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \]  
**Equation (4)**

\[ \text{H}_2\text{S} + 3/2\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} \]  
**Equation (5)**

Combustion products are scrubbed with water. Aqueous acid is introduced next to Westinghouse process producing Sulfuric acid and additional
hydrogen, as given by equation (6):

\[ 2 \text{H}_2\text{O(l)} + \text{SO}_2\text{(aq)} \rightarrow \text{H}_2\text{SO}_4\text{(aq)} + \text{H}_2\text{(g)} \]  

(6)

- Dry Reforming: involves the reaction of the most oxidized form of carbon (CO \(_2\)) with its most reduced form (CH\(_4\)), as shown next:

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \]  

(7)

3. **Non Catalytic Partial Oxidation (NCPO) of Sour Natural Gas**

3.1 **Introduction**

Currently, synthesis gas is produced by steam reforming of sweet natural gas. This is a catalytic process in which the feed gas has to be sulfur free to avoid catalyst poisoning. As a result, acidic gas removal is a prerequisite for the steam-reforming process. H\(_2\text{S}\) is separated from the natural gas by one of the physiochemical separation methods. The separation process is expensive and involves the use of amine solvents. The chemisorption of acidic gas into the solvents is followed by regeneration of these solvents.

Although the bulk production of synthesis gas is done via catalyzed steam reforming of sweet natural gas, non-catalyzed partial oxidation of sour natural gas with appropriate conditions may prove to be more attractive. Simulation work was done by the author and coworkers [1] proposing the NCPO of sour natural gas, as described next.

3.2 **Process Description**

Sour natural gas and the oxidant are preheated separately up to 1200 °F and 1000 °F respectively, then thoroughly mixed prior to the partial oxidation that takes place in the combustion chamber.

The mechanism of the reactions is very complex, but this behavior is consistent with the two-stage-combustion-chamber mechanism, shown in Fig. 3. It involves complete combustion in the first stage via the highly exothermic reactions. A large surplus of methane remains unreacted. This surplus methane can then react with either of the products of the primary reactions in the second stage.

Parametric investigation for NCPO of sour natural gas was carried out using AspenPlus. In this study, the following parameters were considered: effect of the equivalence ratio \((\text{O}_2/\text{CH}_4)\), effect of the hydrogen sulfide content in the feed and effect of the preheat temperature. The optimum conversion of the sour natural gas is achieved in the vicinity of 1/2 molar equivalence ratio depending on the content of hydrogen sulfide in feed of sour natural gas, as illustrated in Fig. 4 & 5 [1,21].

3.3 **Modified Westinghouse Sulfur Process (MWSP)**

It is anticipated in this NCPO, to introduce the absorbed SO\(_2\) into a MWSP. It is one-step electrolysis process for decomposing water into hydrogen and oxygen. Sulfurous acid and water are electrolyzed to produce to H\(_2\) and H\(_2\text{SO}_4\). Although electrical power is required in the electrolyser, much smaller quantities than those necessary in conventional electrolysis are needed. The theoretical voltage to decompose water is ~1.23V, with many commercial electrolyzers requiring over 2.0V. The power requirements (0.17 Volts at unit activity for reactants and products) are thus seen to be less than 15% of those required in a conventional electrolysis [20]. This dramatically changes the theoretical heat and work required to decompose water and leads to high thermal efficiencies. Reaction is given by equation (8):

\[ \text{SO}_2\text{(aq)} + 2\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_4\text{(aq)} + \text{H}_2\text{(g)} \]  

(8)

This is an open cycle, with a continuous feed input (aq.SO\(_2\)).[23]. It is different from the closed cycle described in the literature [22]. The modified proposed process is illustrated in Fig. 6.

4. **Proposed Process Scheme for Reforming Sour Natural Gas**

The following three key elements form the basis for the proposed process configuration:

- The simulation work described before on non-catalytic partial oxidation (NCPO).
- The modified Westinghouse Sulfur Process (MWSP)
- The use of the porous media combustion (PMC) concept, replacing the combustion chamber simulated in the work on NCPO.

4.1 **System Description**

A two-stage mechanism for the NCPO of sour-methane was presented earlier in the simulation model by the author and coworkers. It is based on using combustion chamber (CC) in the reforming process. The proposed model is a sort of visionary reforming process that utilizes porous medium combustion (PMC), instead of combustion chamber (CC), to handle the case of sour natural gas. Using PMC in the reforming of sour natural gas is justifiable because of the voluminous literature published. PMC, also known as filtration combustion: is defined as the process in which a self-sustaining exothermal reactive wave propagates over a porous reagent by means of gaseous oxidizer filtration through an inert solid matrix towards the reaction zone.

The following are some of the main features reported on PMC used in reforming natural gas in general.

1st - Porous media provides increased stability and allows higher mass flow rate compared to laminar premixed flames.
2nd - Maximum temperatures inside the reactor are higher than the adiabatic flame temperature or super-adiabatic due to effective heat re circulation.

3rd - These super a diabatic temperatures drive the reactions of mixtures beyond the conventional flammability limit making ultra-rich combustion possible.

4th - The two stage mechanism proposed for the NCPO of sour gas using the (CC), is in agreement with PMC. Kennedy et. al.[14]. They reported that partial oxidation occurred in two stages when reacting methane (non-sour) and air. In the first stage, methane thermally decomposed when the porous media was at high temperatures. Oxygen was then rapidly consumed which was followed by fast hydrogen production and water. This stage accounted for the majority of the fuel conversion. The second stage was simply, steam reforming, where methane reacted with water to produce hydrogen and carbon monoxide.

5th - Computations carried out by Dhamrat and Ellzey [10] indicated that conversion of methane to hydrogen occurred in two regimes, in support of previous findings.

6th - Extensive experimental and numerical studies on the generation of hydrogen-rich gases from hydrocarbons by superadiabatic partial oxidation have been carried out and have shown the high potential of this approach.

4.2 Schematic Proposed Flow Diagram

Modification is made for the NCPO of sour natural gas [1], replacing the combustion chamber (CC) by PMC reformer as illustrated in Fig. 7. The proposed PCM reformer is taken after Kennedy [12]. Other units will remain basically the same.
5. Conclusions

The question one may ask: why this pathway of NCPO of sour natural gas is considered? The answer is found along the following lines. The combustion of hydrogen sulfide into sulfur dioxide and, hence, sulfuric acid along with the production of synthesis gas via NCPO offers a novel scheme that could compete with the conventional steam reforming. The elimination of both the expensive gas desulfurization process and the steam generation are obvious advantages. NCPO could be described as a self-sufficient steam producer for the reforming reaction.

Using the NCPO of sour natural will lead eventually to convert H2S directly to sulfuric acid rather than elemental sulfur. The acid is produced via the Westinghouse cycle. This represents a different approach from the current technology using Clausis process.

Coupling the NCPO with combustion in porous media (CPM) offers an attractive technology to reform sour natural gas. Systems using porous media in gas reforming enjoy higher power density, extremely good thermal conductivity, and higher efficiency of transforming fuel into energy.

The potential of implementing this scheme in the future, particularly for oil-producing countries, should be considered by carrying out experimental work on the NCPO of sour natural gas, as presented in the proposed scheme described above.

References


