SINGLE STEP COMPACT STEAM METHANE REFORMING PROCESS FOR HYDROGEN-CNG (H-CNG) PRODUCTION FROM NATURAL GAS

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ABSTRACT

Compressed natural gas (CNG) is being increasingly used as a clean transportation fuel. However, for further reduction in emissions, particularly NOx, H-CNG mixture with ~ 20 % hydrogen is recommended. Presently, most of the H-CNG mixture is produced by blending hydrogen with CNG. For hydrogen production, Steam Methane Reforming (SMR) is a major process accounting for more than 90% of hydrogen production by various industries. In this process, natural gas is first reformed to syn gas under severe operating conditions (Pressure 20-30 bar, temperature 850-950 deg C) followed by conversion of CO to hydrogen in the shift reactor. Other method of hydrogen production, such as electrolysis of water, is more expensive. Further, there are issues of safety with handling of hydrogen, its storage and transportation for blending.

In order to overcome these problems, a single step compact process for the production of H-CNG gaseous mixture through low severity steam methane reforming of natural gas has been developed. It employs a catalyst containing nickel, nickel oxide, magnesium oxide and silica and has the capability of producing H-CNG mixture in the desired proportion containing 15-20 vol % hydrogen with nil CO production. The process is flexible and rugged allowing H-CNG production as per the demand. The gaseous H-CNG product mixture can directly be used as automobile fuel after compression. The process can help as important step in safe transition towards hydrogen economy. A demonstration unit is being set up at IOC R&D Centre.

1.0 INTRODUCTION

Compressed natural gas has been steadily gaining popularity as transportation fuel of choice due to its clean combustion characteristics and lower emissions. To improve the air quality further, it is desirable to reduce NOx emissions by blending hydrogen with CNG. Addition of Hydrogen in natural gas even in small quantities (5-20 by volume) results in better combustion of the fuel in internal combustion engines. Combustion of H-CNG blend is more stable than the natural gas alone resulting in increased efficiency and lower emissions. There is an increase of ~ 7-8 % in efficiency, ~ 20-22 % reduction in HC emissions, ~30-35 % reduction in NOx and ~ 15-20 % reduction in CO2. The conventional process involves production of pure hydrogen, its compression, storage and then blending it with CNG to produce H-CNG of desired composition. Steam methane reforming of natural gas or naphtha is the most widely used process for commercial production of hydrogen. This reforming process operates at very high severity where the reaction temperatures are in the range of 850-950 deg C and pressures in the range of 20-30 bar. The reforming reactor consists of multiple tubes packed with reforming catalysts and are exposed to such high reaction temperatures requiring very exhaustive and expensive metallurgy. The exit gases from this high severity reformer consists of substantial amounts of carbon monoxide (CO) which requires further conversion of CO to hydrogen in the downstream Shift Reactors using water gas shift reaction. Further the pure hydrogen is obtained by employing pressure swing adsorption (PSA) system downstream of shift reactors for removal of contaminants from hydrogen. These multiple reaction steps make the pure hydrogen production process quite complex and expensive.

These problems such as separate production of pure Hydrogen through complex high severity reforming process, compression and storage of pure hydrogen and blending with CNG have been overcome by developing a single step compact process for the production of H-CNG gaseous mixture through low severity steam methane reforming of natural gas.

The main advantages of the developed process are

- It eliminates need for separate production of pure Hydrogen, its compression and storage
- The process operates at very mild operating conditions therby allowing use relatively simpler and less expensive metallurgy
- It employs simpler fixed bed reactor
- CO is not present in the reactor effluent and thus does not need further shift conversion
- Proces is capable of producing H-CNG gaseous mixture of desired composition for direct dispnsing as automobile fuel
- The process has been designed in such a way that it is safe, rugged and flexible for quick start and stop to meet H-CNG demand fluctuations for dispensing to automobiles.

2.0 EXPERIMENTAL WORK / RESULTS & DISCUSSION

Experiments have been carried out in a fixed bed downflow reforming reactor. The feed for the process is natural gas containing predominately methane and traces of H_2S. The experimental set up and process is schematically illustrated in Figure 1 (Annexure-1). The natural gas stream via line 1 is preheated in heat exchanger 2 by product H-CNG gas stream coming via line 3 from steam methane reformer 4 exit and is fed to the sulfur guard reactor 5. The make up water via line 6 and excess steam condensate via line 7 from the gas liquid separator 8 is fed to the fire box 9 for generating steam. The combined treated natural gas and steam are fed via line 10 to the reformer 4 at reaction temperature of 350-390 deg C. A slip stream of treated natural gas from sulfur guard 5 is fired via line 11 to the fire box for steam generation and heating of the treated natural gas. The flow rate of the slip stream of natural gas to the fire box is controlled via control valve 12 which is cascaded with temperature of catalyst bed in reformer 4. A bypass stream of treated natural gas via line 13 is cascaded through control valve 14 with the combined stream of heated natural gas and steam for controlling inlet temperature to the reformer. The low severity steam methane reforming of natural gas is carried out in the fixed bed vapor phase downflow reformer 4 containing reforming catalyst at a temperature of 350-390 deg C and pressure of 5-7 bar. The H-CNG product gas containing 15-20 vol % hydrogen with nil carbon monoxide after heat exchange in exchanger 2 is fed to the separator 8. The excess steam condensed is recycled back along with make up water. The H-CNG product gas is sent via line 15 to the low pressure storage vessel 16. On-line GC / gas analyzer 17 is provided for analysis of product gas composition and is used for cascading a stream of treated natural gas via line 18 through control valve 19 for adjusting the gas composition in the storage vessel 16. The H-CNG product gas is then compressed in a two-stage compressor 20 and is sent to the high pressure storage vessel 21. A provision of recycling H-CNG product gas from 1st stage of compressor via line 22 through control valve 23 to the reformer is kept for keeping reformer ready in standby mode during period of no demand of H-CNG. The compressed H-CNG product gas is dispensed through dispenser 24 to the vehicles. The H-CNG production can be started and stopped very quickly by cascading with steam flow. It can be directly used as fuel in automobiles after compression without any separation/ purification. The H-CNG gas can be re-circulated to the reformer in absence of H-CNG product demand.

Experimentation was conducted in a fixed bed down-flow reformer using 100 cc catalyst containing nickel, nickel oxide, magnesium oxide and silica. Natural gas containing predominantly Methane and traces of H_2S was used as feed. Sulfur guard catalyst bed was used in upstream reactor to remove H_2S. The summary of operating conditions and composition of H-CNG product gas is provided in Table -1.

Table 1: Operating conditions and product gas composition

Parameters		Product Gas Composition	
Reactor Temperature (^{o} C)	350-400	Component	Vol %
System Pressure (bar)	4-12	H2	15-20
Steam to carbon ratio, molar	1.2-2.0	CH4	70-80
GHSV, dry basis, h^{-1}	1750-2250	CO2	3-5

In order to study the ruggedness of the process involving quick start and stop of the process depending upon the product requirement at fuel station, the catalyst system was subjected to number of on-off cycles for H-CNG production. The reforming reactor was subjected to 15 number of on-off cycles for establishing the ruggedness of the process and quick start and stop of H-CNG production for varying demand of H-CNG to suit the requirements of retail gas station. The re starting time for the process is ~ 1 hour to establish all the operating parameters and obtaining the desired on-spec product composition. The results of the study are given in Table-2.

Table 2: Operating conditions and product gas composition for checking process ruggedness

Experiment → Parameter ↓	Initial Run	Run after frequent start and stop of reforming reactor
Operating conditions		
Reactor Temperature (o C)	390	390
System Pressure (bar)	5	5
Steam to carbon ratio, molar	1.45	1.45
GHSV, dry basis, h-1	2000	2000
Product Composition		
Hydrogen (volume %)	19.95	20.02
CO (volume %)	nil	nil
CO2 (volume %)	4.97	4.95
Methane (volume %)	75.08	75.03

It can be observed from the above results that the process is very rugged and there has been no deactivation of the catalyst even after subjecting it to frequent starting and stopping the conversion in the reforming reactor.

3.0 DEMONSTRATION AND SCALE UP

A demonstration unit of 2.5 Nm3/hr is being installed at IOC R&D Centre. The unit has been designed along with M/s Xytel India Pvt Ltd. The unit has been made compact so that it can be placed in the existing CNG stations. The unit is equipped with following safety features

1. PSV (Pressure Safety Valve) and Rupture disk for safety against overpressurisation
2. Separate vent lines for Low pressure and high pressure vents
3. TSS (Temperature Safety Switches) for safety against overheating
4. Control logic and alarms for necessary corrective actions (including emergency shutdown) in case of process upsets, runaways etc.
5. Leak detection system on the pilot plant skid
6. Nitrogen purging wherever required
7. Scrubbing system for polluting gases such as H_2S, CO_2

In addition the storage of HCNG is being placed in approved and licensed area from explosives department in India

The safety features will help in avoiding any accident as the process technology will be utilised at public accessed CNG stations either at centralised or distributed locations.

It is planned to optimise process conditions in the demo plant and dispense 18% HCNG for trial at IOC R&D. Further based on the studies in the demo unit scale up data will be generated and Basic Design and Engineering Package (BDEP) will be prepared for a commercial unit.

4.0 CONCLUSION

A single step compact process for the production of H-CNG gaseous mixture through low severity steam methane reforming of natural gas has been developed. It has capability of producing H-CNG mixture in the desired proportion containing 15-20 vol % hydrogen with nil CO production. The process is flexible and rugged allowing H-CNG production as per the demand. The gaseous H-CNG product mixture can directly be used as automobile fuel after compression. The process avoids separate handling of hydrogen and CNG at high pressures and hence is much safer than separate production and handling of Hydrogen and CNG

A demo plant equipped with safety measures is being set up at IOC R&D. It is planned to prepare a Basic Design Engineering Package and cost estimates for commercial unit based on the data generated in the demo plant.

Production and use of HCNG will play a very important role in safe shift towards use of “Hydrogen as future fuel”. Single step compact steam methane reformer is a very simple, efficient, safe and economical process and can be utilised on centralised or distributed scale for production and use of HCNG.

Annexure-1

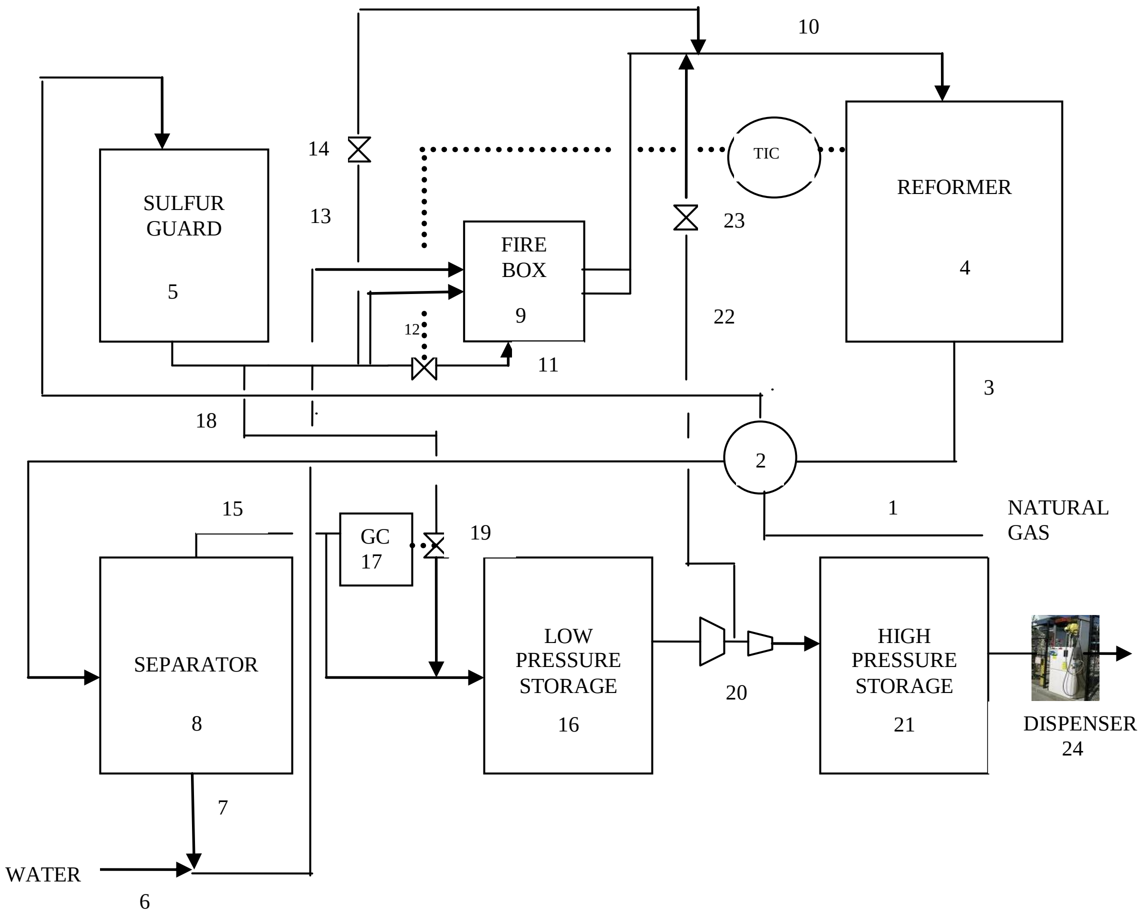

Figure 1: Schematic of H-CNG Process