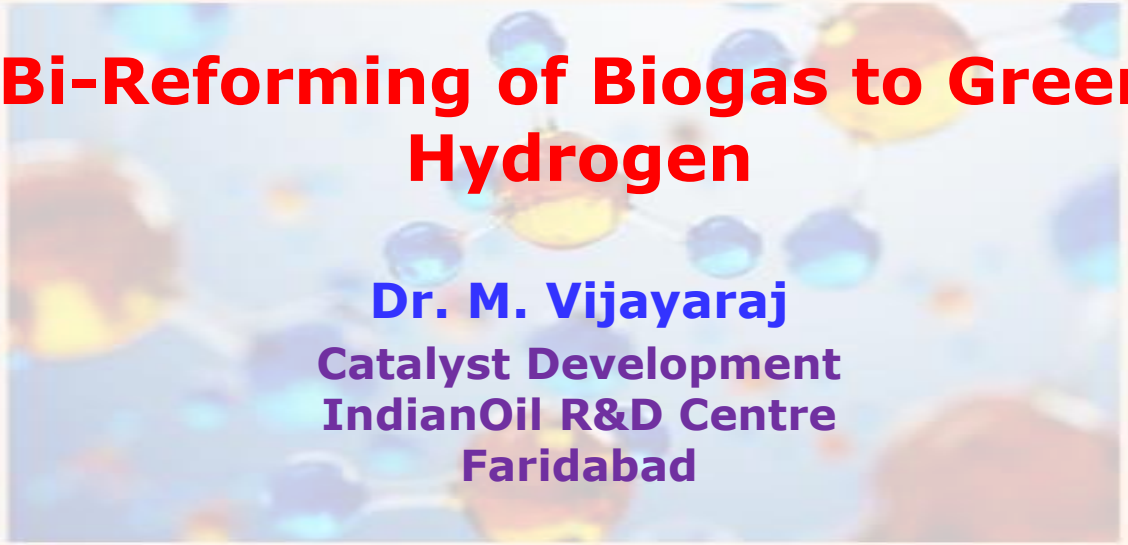
Recent Developments in Catalysis in Process Industry



Bi-Reforming of Biogas to Green Hydrogen

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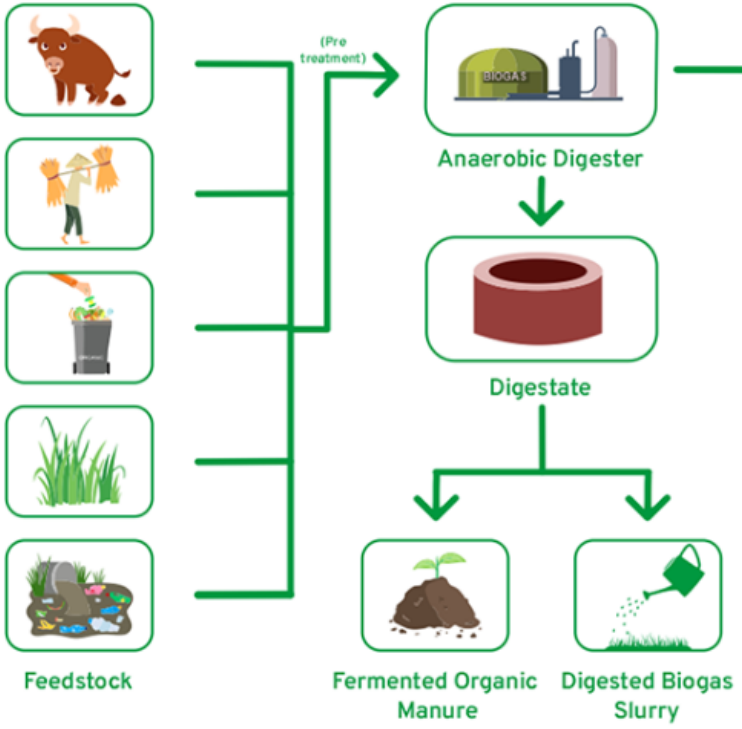
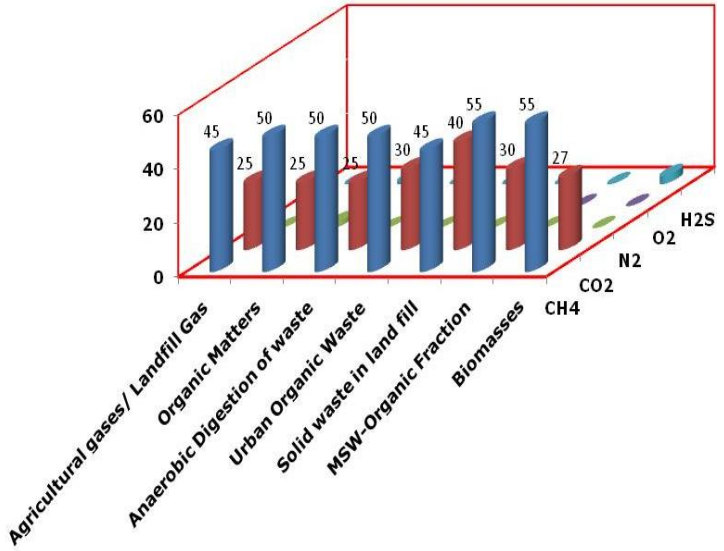
Auditorium, IIChE-NRC
New Delhi

Biogas- An Overview

Complex mixture produced from waste/biomass sources through anaerobic decomposition



CH_4 = 45-70 %
CO_2 = 25-40 %
H_2O = 0-20%
N_2 = 0-25%
O_2 = 0-5%
H_2S = 0-3%
Others = Traces



Composition depends on the feedstock
Methane, CO_2 and other impurities varies cannot be fixed

https://satat.co.in/satat/cbg.html

Biogas from waste – Commercial technology

Conversion of Organic Waste to Biogas through anaerobic digestion technology

IBG Plus – Single stage

- **Single Stage Biomethanation**

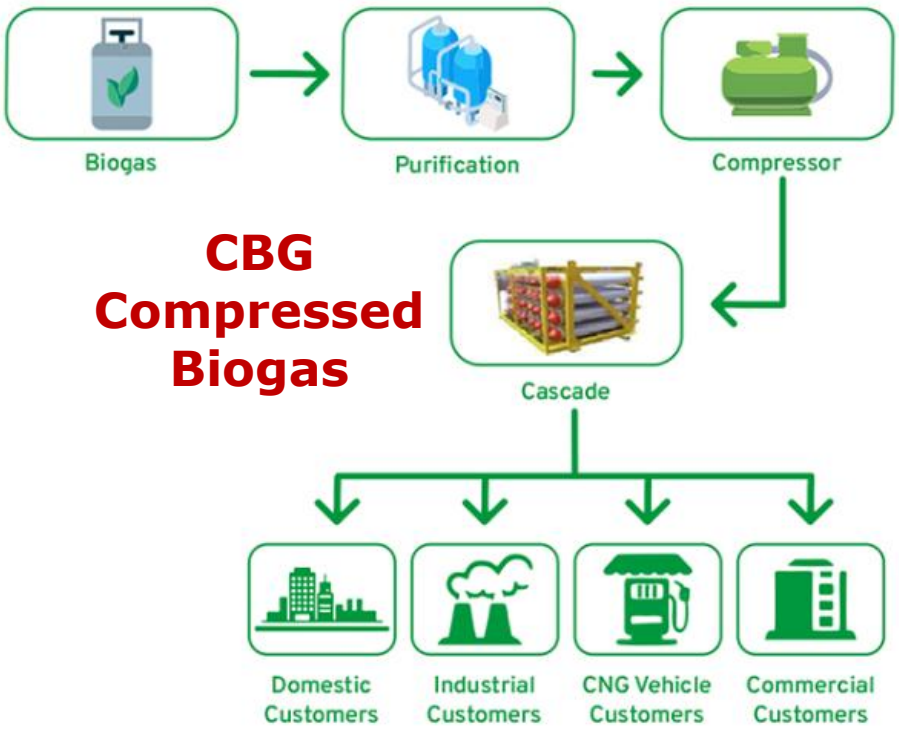
IBG Max – Double stage

- **Double Stage Biomethanation**

- 5 to 240 Tonnes per day processing
- 70-80% methane content
- Proprietary innoculants for efficient conversion under wide range of temperature & salinity

https://iocl.com/pages/licensing-of-technologies

Application of Biogas



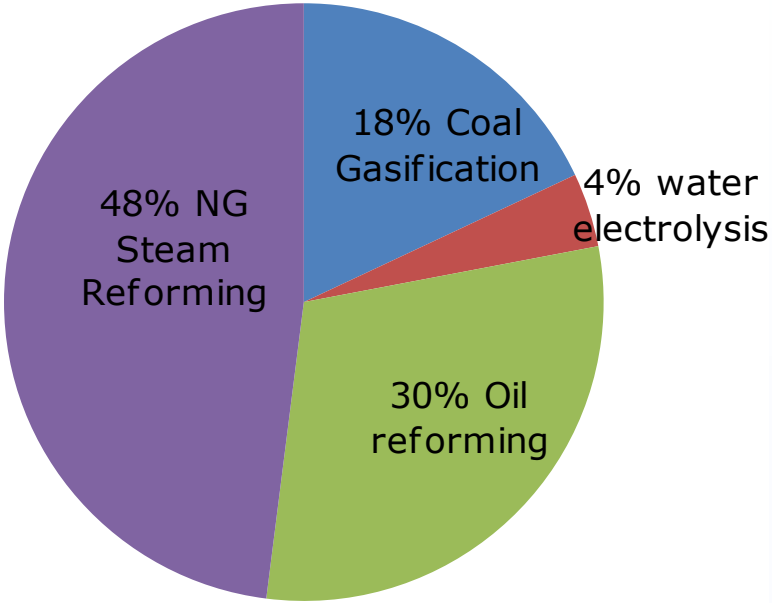
BIS 16087:2016 Specifications of CBG

Characteristics	Requirement
Methane (CH4), Min.	90.0 %
Only Carbon Dioxide (CO_2), Max.	4%
Carbon Dioxide (CO_2)+ Nitrogen (N_2)+ Oxygen (O_2), Max.	10%
Oxygen (O_2) Max.	0.5%
Total 'S' (including H_2S) mg/m^3 Max.	20 mg/m^3
Moisture mg/m^3, Max.	5 mg/m^3

- Calorific value similar to CNG
- Renewable alternate for CNG
- Through SATAT Scheme CBG procurement & distribution facilitated

https://satat.co.in/satat/cbg.html

Hydrogen production



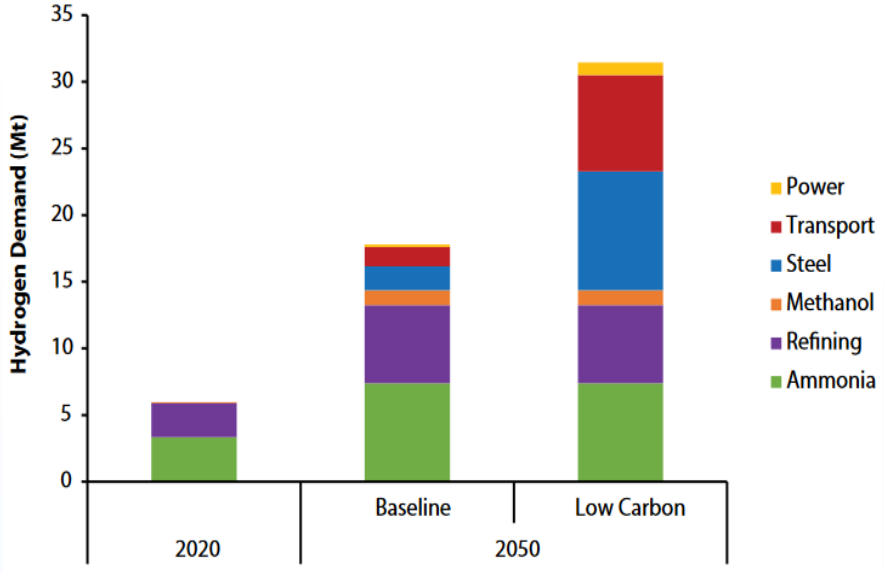
- H_2 is mostly produced through reforming of Oil & Natural Gas/Coal
- Environment concern due to high carbon intensity processes
- Approx 10 folds CO_2 emitted per unit production

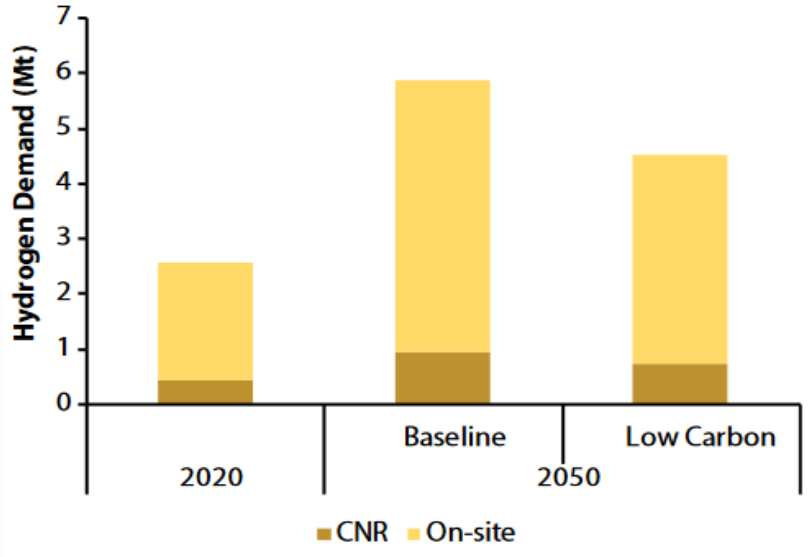
  10.69 kg CO_2 e/ kg H_2
- Decarbonization targets are set by adopting CCUS

  ≈ 3 kg CO_2 e/kg H_2
- Focus on other sustainable technologies increased especially water electrolysis

Zhao et al., iScience 23, 2020, 101082

H_2 Requirement in India



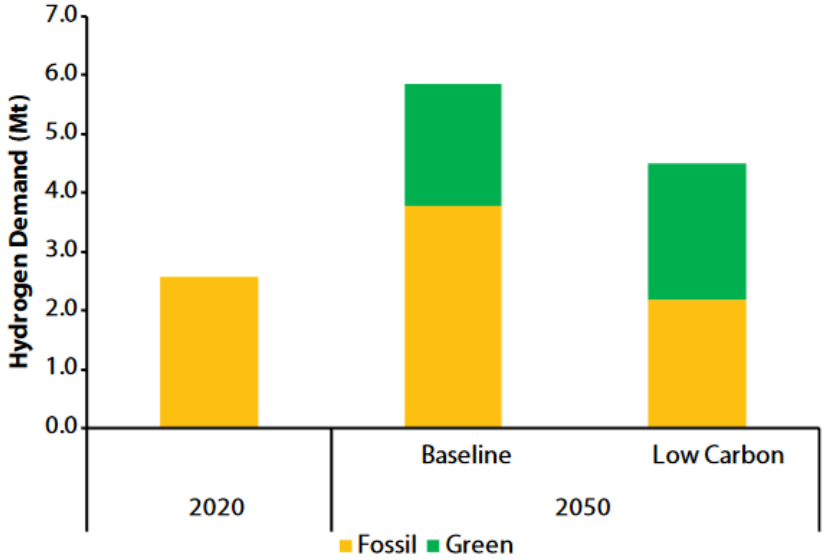


- Power and transport will compete with other sectors
- With Low carbon foot print, demand will manifold except in refineries

- ✓ H_2 demand increase by 2 fold (6MMT) due to low 'S' fuels requirement
- ✓ Low carbon scenario, demand is only 5MMT due to FCVs & EVs growth & less fuel demand

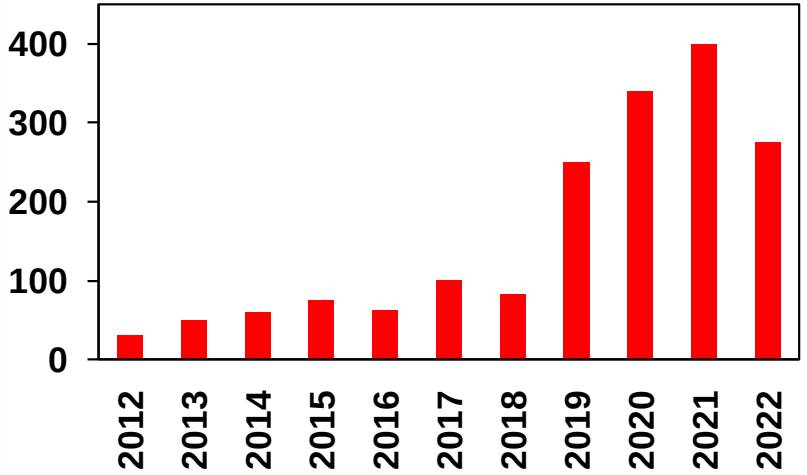
Source: TERI Report

Low Carbon Intensity Route



- Govt. Mandate, Green H_2 (G-H_2)displace NG-based H_2 by 2030 & reach 30% share by 2050
- In low carbon scenario demand share increase up to 50% by 2050

Growing focus on biogas to H_2



- Water electrolysis is most matured technology to produce Green H_2
- High cost & large quantity of water required
- Biogas Reforming to produce green hydrogen
- Renewable and carbon neutral process

Zhao et al., iScience 23, 2020, 101082

Methane Reforming

Process Type	Reaction
Partial Oxidation POX	$CH_4 + ½\ O_2 \rightarrow CO + 2H_2$
Steam Reforming SR	$CH_4 + H_2O \rightarrow CO + 3H_2$
Autothermal Reforming ATR	$2CH_4 + O_2 + CO_2 \rightarrow 3H_2 + 3CO + H_2O$ $4CH_4 + O_2 + 2H_2O \rightarrow 10H_2 + 4CO$
Dry Reforming DR	$CH_4 + CO_2 \rightarrow 2CO + 2H_2$
Bireforming SR + DR	$CH_4 + H_2O \rightarrow CO + 3H_2$ $CH_4 + CO_2 \rightarrow 2CO + 2H_2$
Trireforming TR	$CH_4 + H_2O \rightarrow CO + 3H_2$ $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ $CH_4 + ½\ O_2 \rightarrow CO + 2H_2$

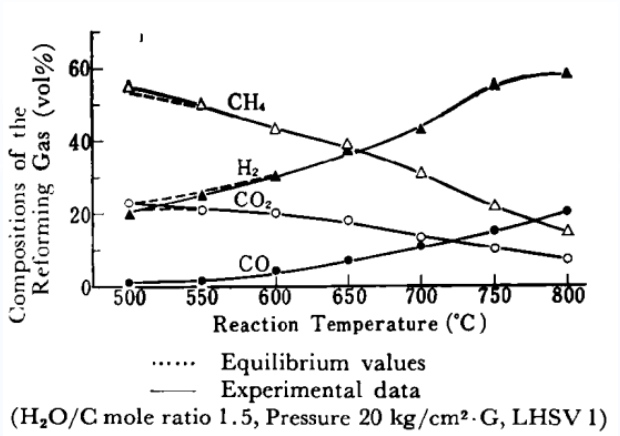
Chen et al., Catalysts 2020, 10, 858

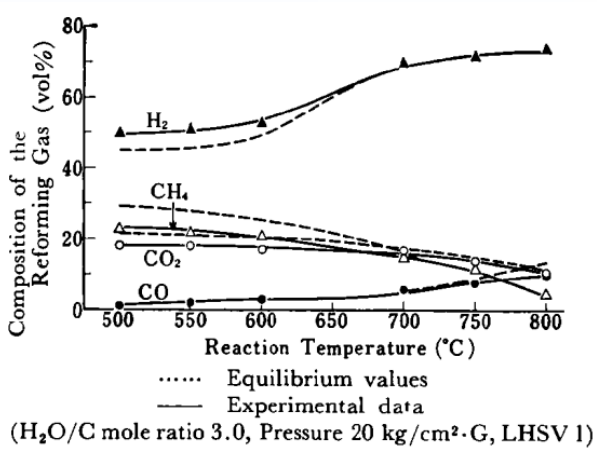
Steam Reforming of Methane

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad +206\ kJ/mol$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad -41\ kJ/mol$$

- SR –endothermic; WGS – mildly exothermic
- Steam to Methane ratio 2.5-3 for complete conversion and maximum H_2 yield and also coke removal





R/O Temp. 800-900°C
Pressure 20-30 bar
S/C = 2.5-3.0
H_2/CO = 2 – 4

✓ Increasing steam to carbon ratio and Reforming temp. H_2 yield increased along with conversion

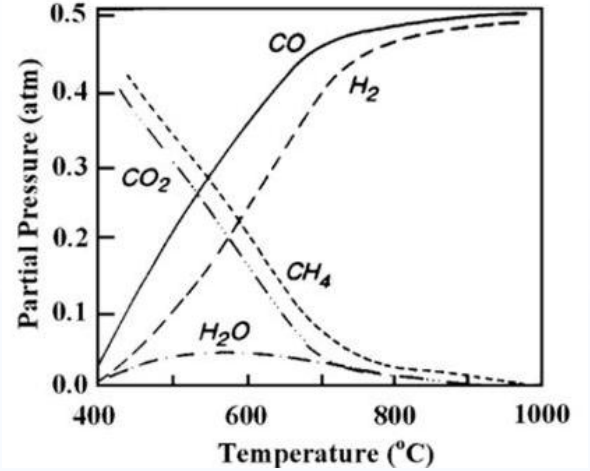
Komatsu & Yamaguchi, Bull. Jpn. Pet. Inst., 16 (2), 1974, 99

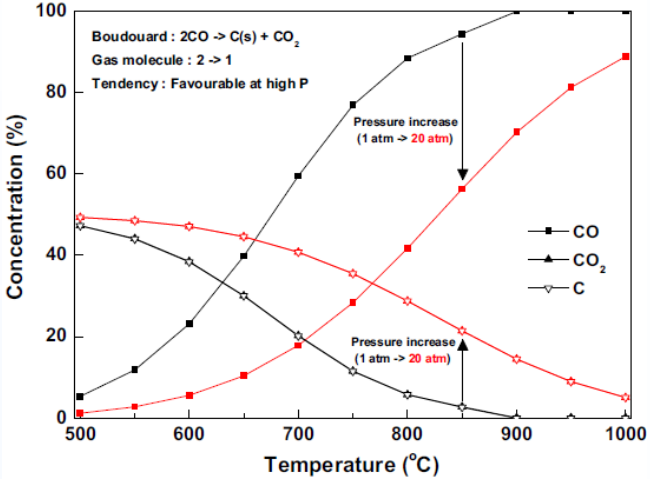
Dry reforming of Methane

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ +247 kJ/mol

$2CO \rightarrow C + CO_2$ - 172 kJ/mol

$CH_4 \rightarrow C + 2H_2$ +75 kJ/mol





R/O Temp. 800-1000°C

Pressure 1-20 bar

CH_4/CO_2= 1

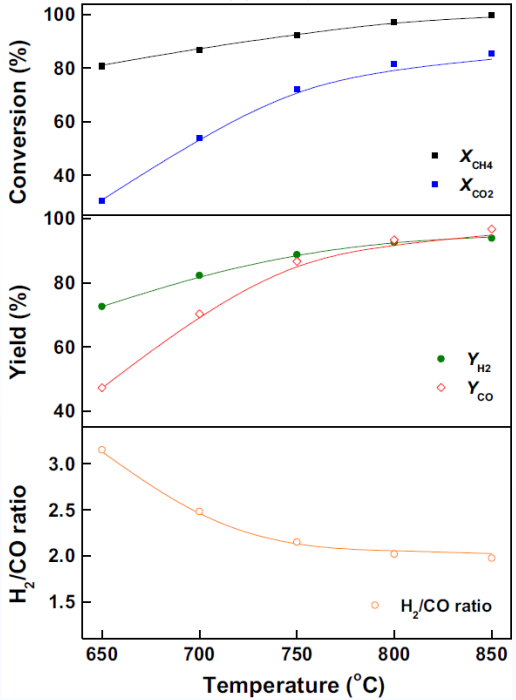
$H_2/CO \leq 1.0$

Highly endothermic, operated at >850° C for maximizing conversion

Coke formation inhibited by reducing reaction pressure and increasing CO_2/CH_4

Li et al., J. Mat. Chem. A., 9, 2021, 12495

Bi-reforming of Methane



$CH_4 + H_2O \rightarrow CO + 3H_2$ +206 kJ/mol

$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ +247 kJ/mol

R/O Temp.(800-950°C)

Pressure 20-40 bar

S/C < 1.8

H2/CO ≤ 3

$CH_4:H_2O:CO_2 = 1$

$(H_2O+CO_2)/CH_4 = 1.2$; $H_2O:CO_2 = 1\text{-}2.1$

CH_4 & CO_2 both GHG can be converted to valuable products

$H_2/CO \leq 2$ at above 800° C as CO_2 conversion increases

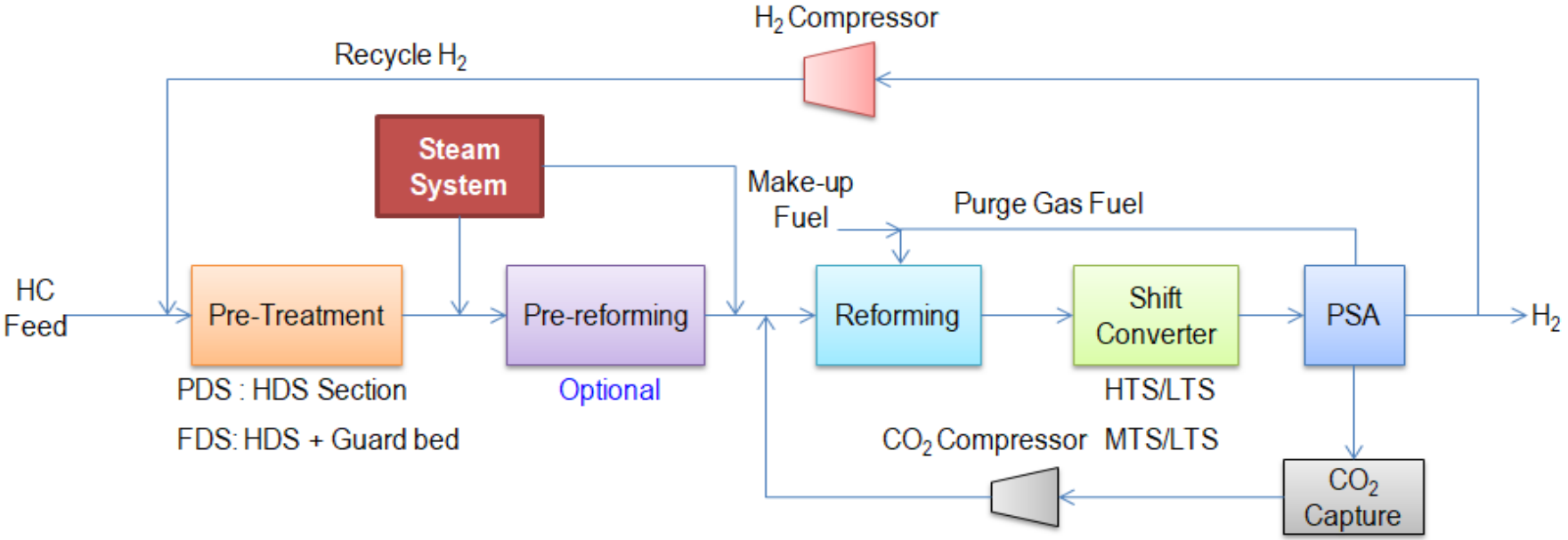
Jang et al., Appl. Energy, 173, 2016, 80

Methane Reforming - Comparison

	Advantages	Carbon Intensity
Steam Reforming SR	Commercially operated, Best H_2/CO production	**High**
Dry Reforming DR	100% CO_2 conversion, GHG consumption	**Lowest**
Bi-Reforming SR + DR	Best H_2/CO for production of fuel, coke reduction, lower carbon footprint	**Low**

Dry reforming & Bi-reforming are attractive for Biogas conversion due to consumption of CO_2 present in it

Hydrogen Production Unit



With modification to the existing unit, biogas reforming can be done

Summary

- Biogas reforming to Green Hydrogen- abatement of GHG emission
- Impurities removal to limit catalyst poisoning – Cost inhibiting purification steps not required
- Product yield H_2/CO >1
- CO_2 utilized for reforming process
- Under tuned operating condition, coke deposition minimized to acceptable limit or catalyst longevity maintained
- Required minor modification to existing plant with optimal cost implication

Thank you