Dry Reforming-Fischer-Tropsch Synthesis-Catalytic Dehydrogenation: A method to No flaring-No CO_2 emission in Gas Refinery

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17-Sep-2014

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Green House Emission

- 139 billion m3 of gas is flared annually

Major green house gases:

- CO_2 : 9–26%
- CH_4: 4–9%
- Ozone, which contributes 3–7%

Other source of pollutants :

- particulate soot
- oxides of nitrogen (NOx)
- sulfur oxides (SOx)
- volatile organic compounds (VOCs)
- unburned fuel
- undesirable by-products of combustion

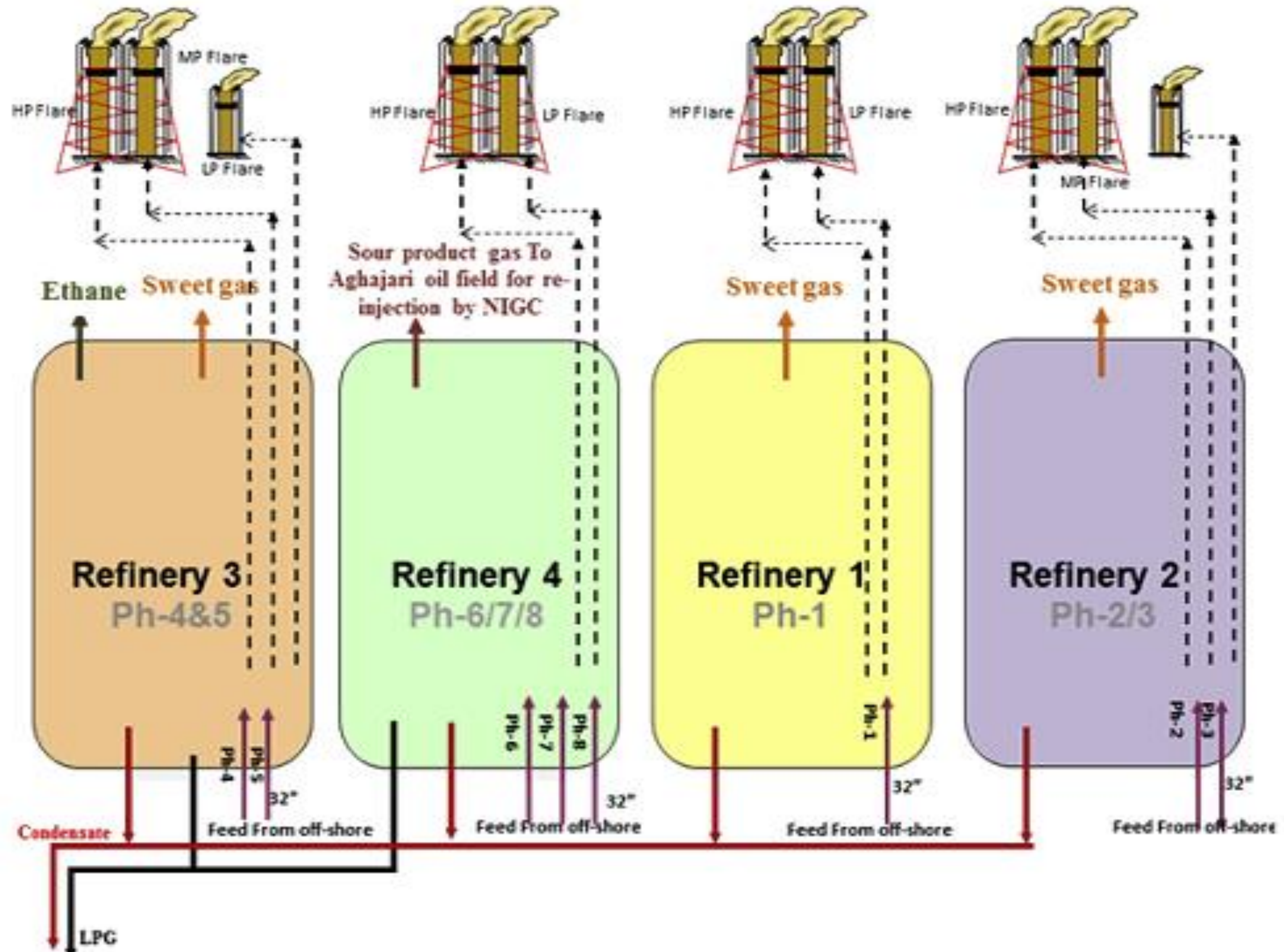


Fig 1. The configuration of domestic gas processing plants.

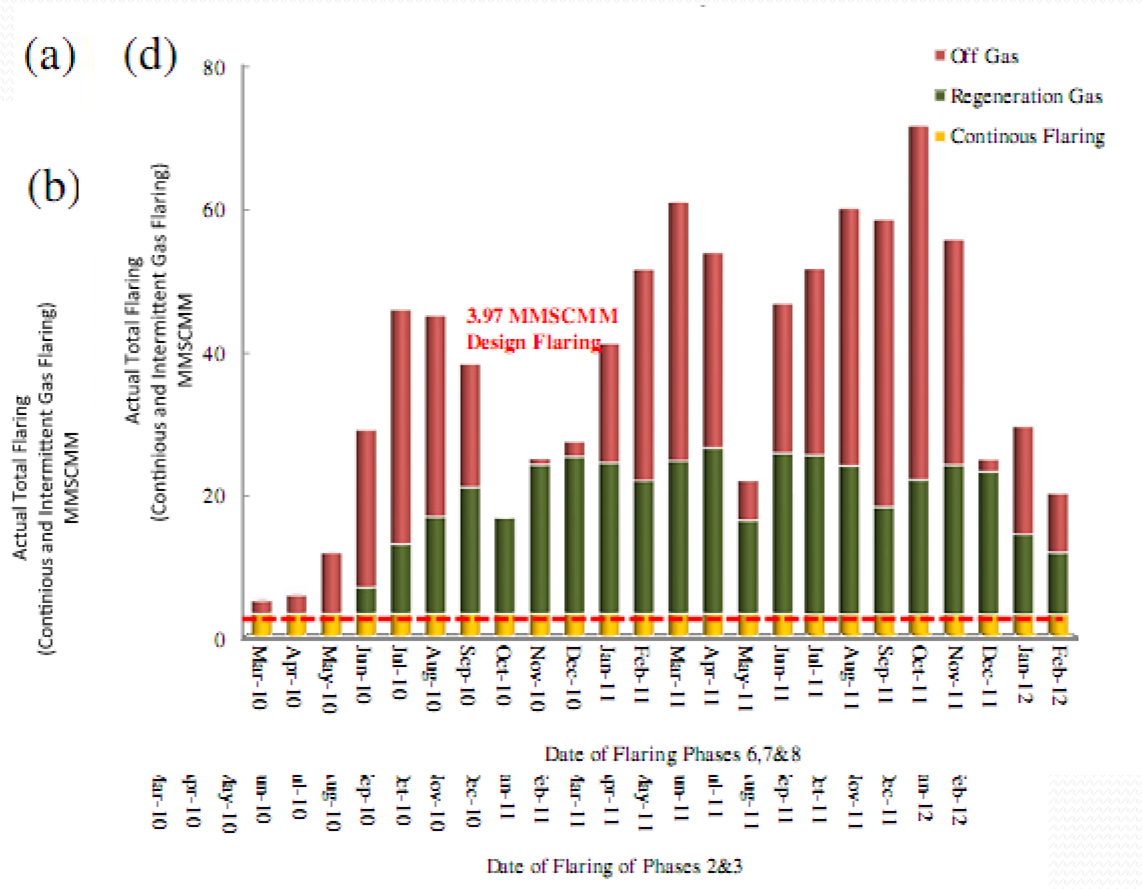
Gas flaring in South Pars Gas Complex

Refinery 1

Refinery 2

Refinery 3

Refinery 4



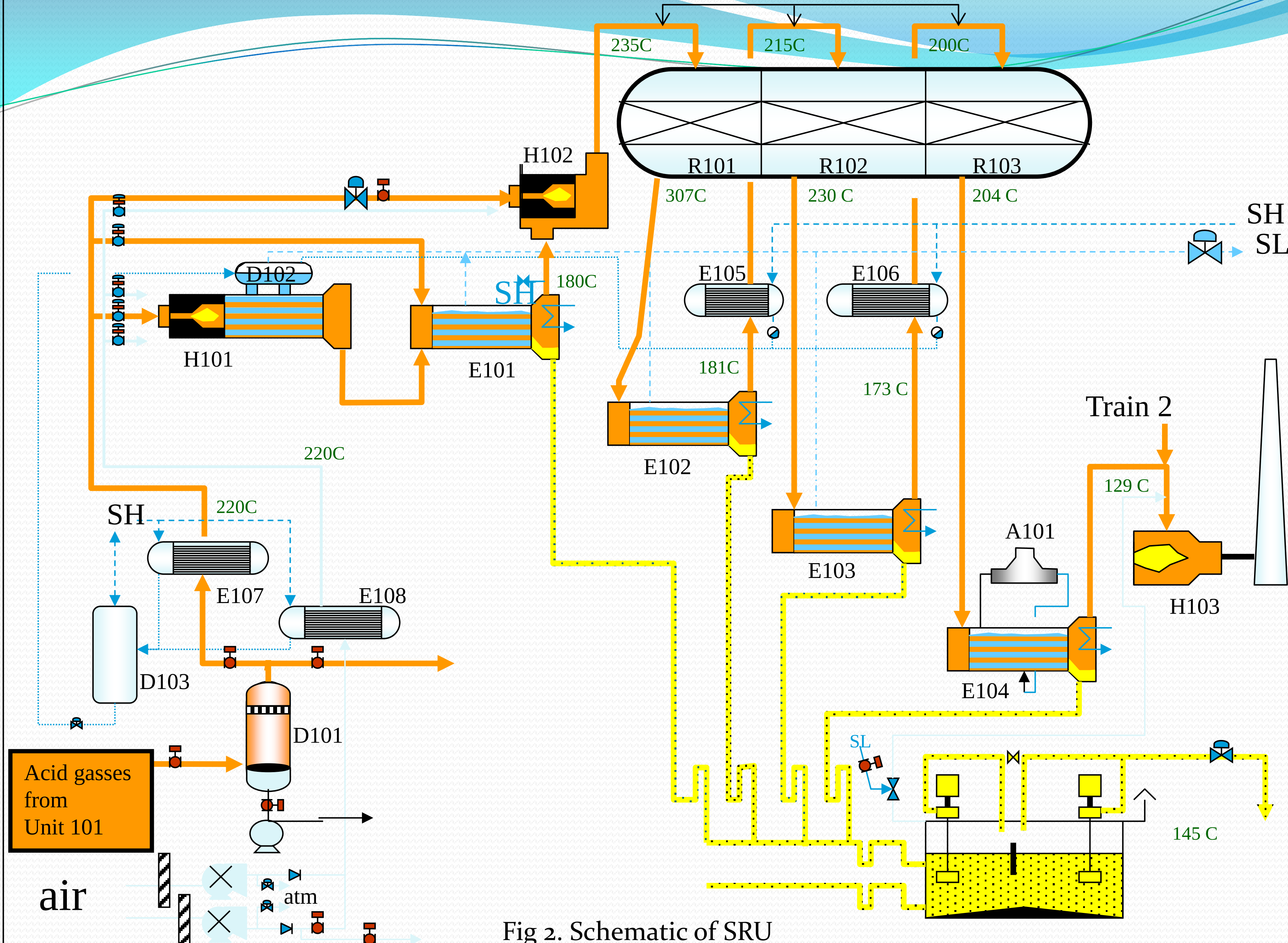


Fig 2. Schematic of SRU

Claus Reactions

$H_2S + 3/2\ O_2 \rightarrow H_2O + SO_2$ (combustion of acid gas)

$2\ H_2S + SO_2 \leftrightarrow 2\ H_2O + 3/2\ S_2$ (CLAUS reaction)

Flare gas composition

Table 1. Composition of Flare Gas

Component	Mol Fraction
Methane	0.87264
Ethane	0.055636
Propane	0.020457
N_2	0.036381
CO_2	0.000498
Butane	0.009644
Pentane	0.003508
H_2S	0.000000
H_2O	0.001221

Flue gas composition

Table 2. Flue Gas Composition

Component	Mol Fraction
CO_2	0.256142
SO_2	0.004456
H_2	0.006695
CO	0.004115
O_2	0.01
N_2	0.476591
H_2O	0.242

Gas to Liquid Technology

- The world energy crisis
- High oil prices
- Environmental pollution

Gas To Liquid (GTL) technology

to

Manufacture of transportation fuels

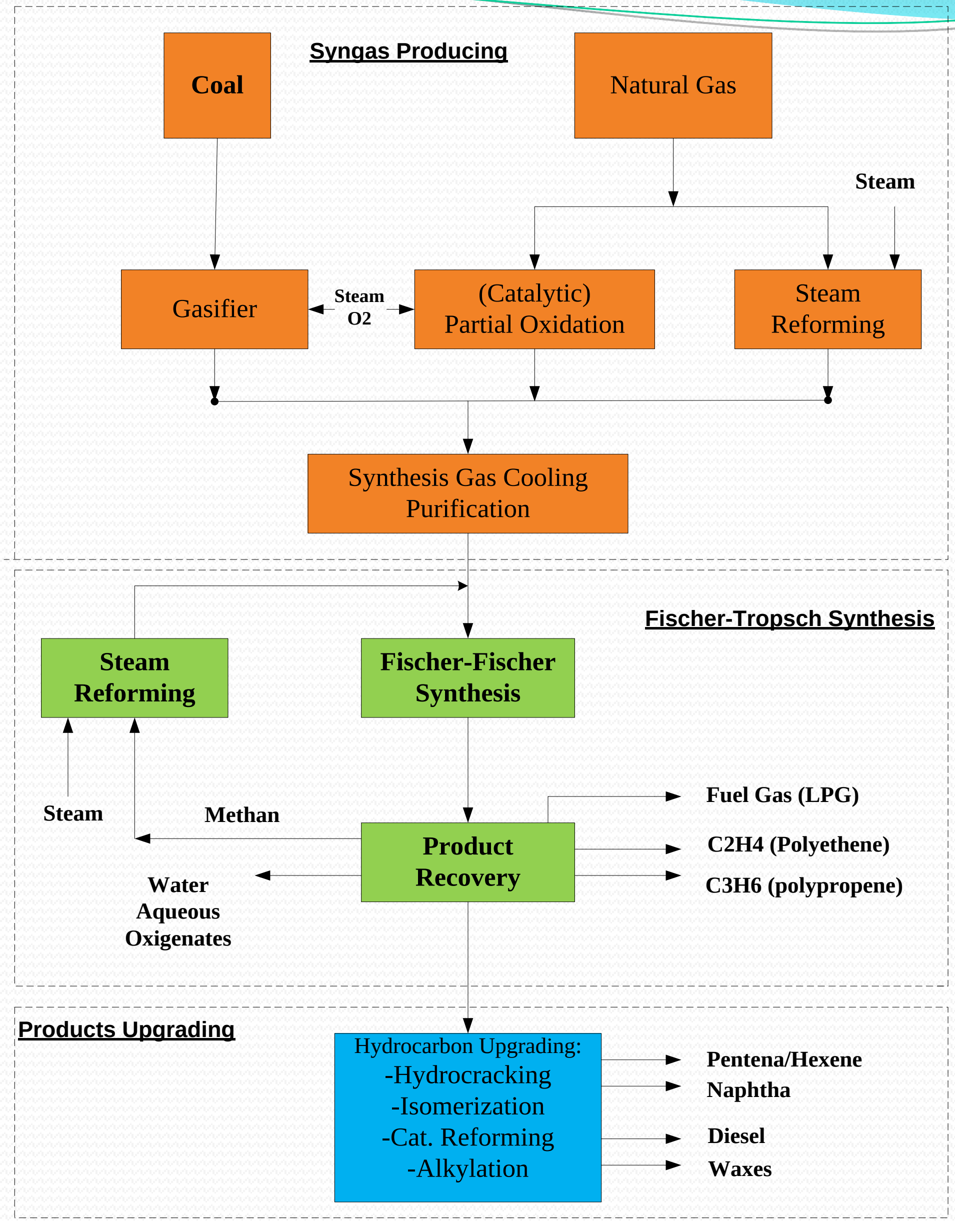


Fig 3. Schematic of typical GTL technology

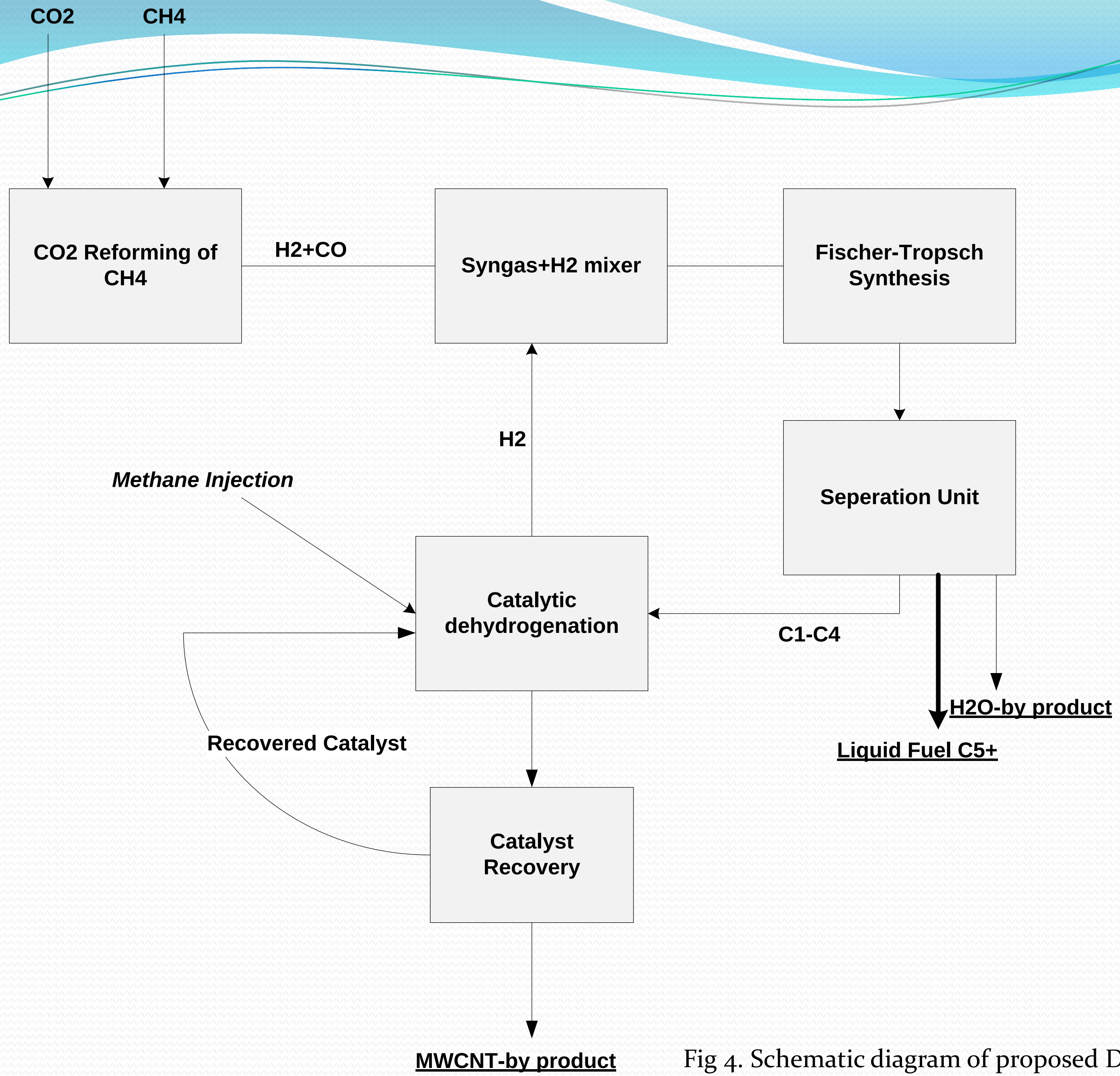


Fig 4. Schematic diagram of proposed DRM-FTS-CDH-MI system.

Process outline

Reforming of Methane

- Steam reforming

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2, \Delta H_{298K} = 206 kJmol^{-1}$$

- Partial oxidation reforming

$$CH_4 + 0.5O_2 \Leftrightarrow CO + 2H_2, \Delta H_{298K} = -35.9 kJmol^{-1}$$

- CO_2 reforming

$$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2, \Delta H_{298K} = 247 kJmol^{-1}, \Delta G^{\circ}_{298K} = 61770 - 67.32T$$

Steam reforming

- Steam reforming is the most widely used technology for methane-based syngas production.
- Drawbacks:

  - High H_2/CO ratio≈3
  - Excess steam to avoid carbon deposition on the catalyst.
    higher operation cost
  - High temperature tubular heat exchanger reactor
    higher Capital cost
  - Production of CO_2 with syngas

  The removal and disposal of CO_2 is another major issue.

Partial oxidation reforming (POM)

- Syngas with a H_2/CO ratio of 2
- Mildly exothermic process

- Non-catalytic and catalytic process

Non-catalytic

Operated under the conditions of 30-100 atm and around 1573K.

- High temperature

Catalytic process

- Lower temperature
- Efficiency and Economics
  - Short duration time

CO_2 reforming

- Lower theoretical H_2/CO ratio
- Reuse of CO_2

Most difficult problem

- Carbon deposition through methane decomposition
- Boudouard reaction which rapidly deactivates the catalyst

$$2CO \Leftrightarrow CO_2 + C, \Delta H_{298K} = -171 kJmol^{-1}, \Delta G^{\circ}_{298K} = -39810 + 4.87T$$

catalyst development major aspect of research in this area

Catalyst for CO_2 reforming of Methane

Metal + Support+Promoter

- Role of Metal
  - CH4 adsorbed on the metal in a dissociated form to produce hydrogen and a hydrocarbon species CHx (x=0–4)

  Values of x dependent on:
  - Metal substrate
  - Reaction temperature

- VIII (ruthenium)
- IX (cobalt, rhodium, iridium)
- X (nickel, palladium, platinum)

    - Ni-based catalysts: resistant to carbon deposition and high activity for reaction.

Catalyst for CO_2 reforming of Methane

Metal+**Support**+Promoter

- Role of Support
  - distinct behavior in catalytic reactions
  - resistance to carbon deposition.

- Acidic Support-------SiO_2
- Basic supports--------Al_2O_3

Catalyst for CO_2 reforming of Methane

Metal+Support+**Promoter**

- Role of Promoters
    - Improving the coke resistance
    - Enhance the activity of reactions

- Textural
- Chemical
    - Alkali----------------------------------K
    - Alkaline earth meal-----------------Ca

Mechanism for the CO_2 Reforming of Methane

Catalyst component	Proposed mechanism
Metal active site ($M_{(as)}$)	$CH_4 + 2\,M_{(as)} \rightleftharpoons CH_3{-}M_{(as)} + H{-}M_{(as)}$ $CH_3{-}M_{(as)} + M_{(as)} \rightleftharpoons CH_2{-}M_{(as)} + H{-}M_{(as)}$ $CH_2{-}M_{(as)} + M_{(as)} \rightleftharpoons CH{-}M_{(as)} + H{-}M_{(as)}$ $CH{-}M_{(as)} + M_{(as)} \rightleftharpoons C{-}M_{(as)} + H{-}M_{(as)}$ $2\,H{-}M_{(as)} \rightleftharpoons H_{2(g)} + 2\,M_{(as)}$
Support	Acidic support: $CO_{2(g)} \rightleftharpoons CO_{2(metal)}$ $CO_{2(metal)} \rightleftharpoons CO_{(metal)} + O_{(metal)}$ $CO_{(metal)} \rightleftharpoons CO_{(g)}$ Basic support: $CO_{2(g)} \rightleftharpoons CO_{2(support)}$ $CO_{2(support)} + O^{2-}_{(support)} \rightleftharpoons CO^{2-}_{3(support)}$ $2\,H_{(metal)} \rightleftharpoons 2\,H_{(support)}$ $CO^{2-}_{3(support)} + 2\,H_{(support)} \rightleftharpoons HCO^{-}_{2(support)} + OH^{-}_{(support)}$ $CO_{(support)} \rightleftharpoons CO_{(g)}$
Promoter	$CO_{2(g)} \rightleftharpoons O_{(promoter)} + CO_{(support)}$ $O_{(promoter)} + C_{(metal)} \rightleftharpoons CO_{(g)}$

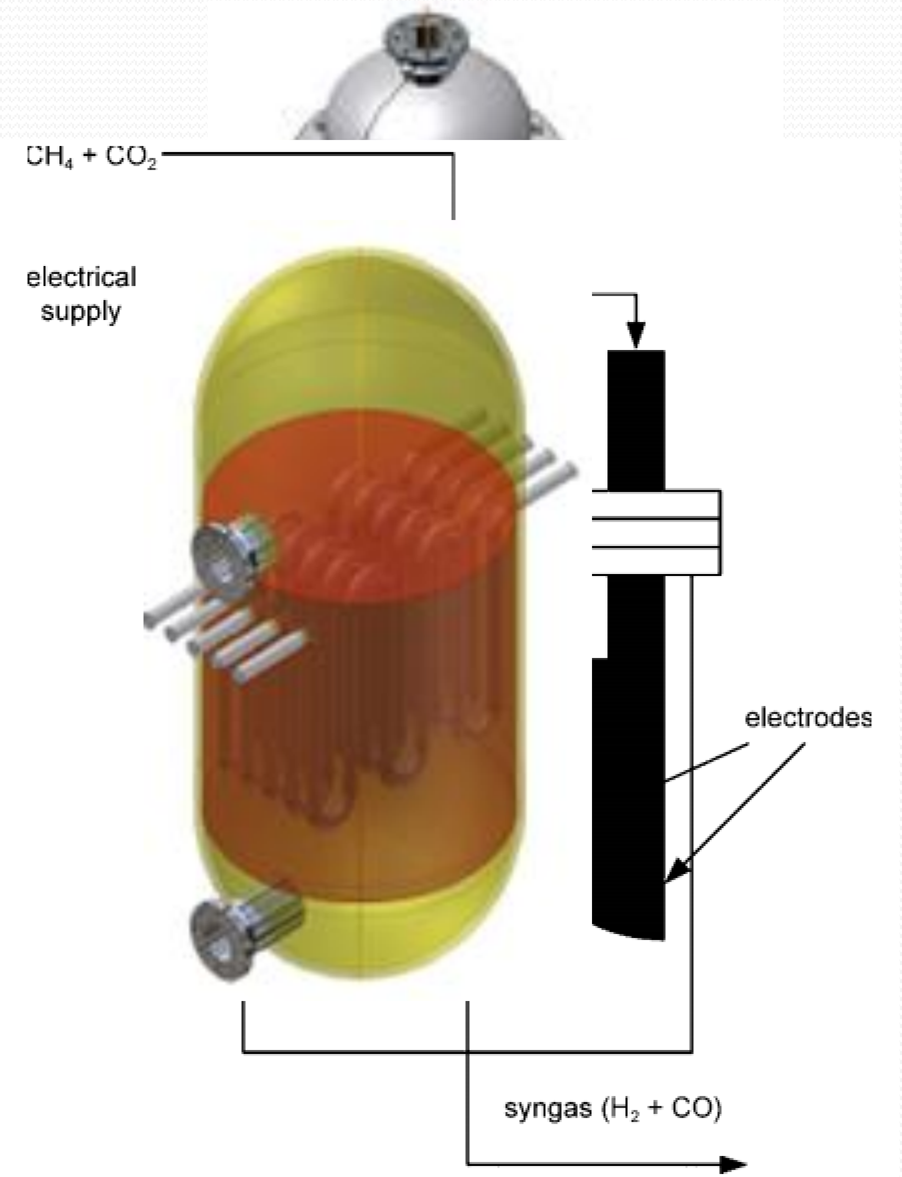
Adsorption $CH_4 + M_{(as)} \Leftrightarrow M_{(as)} - CH_3 + H_2$

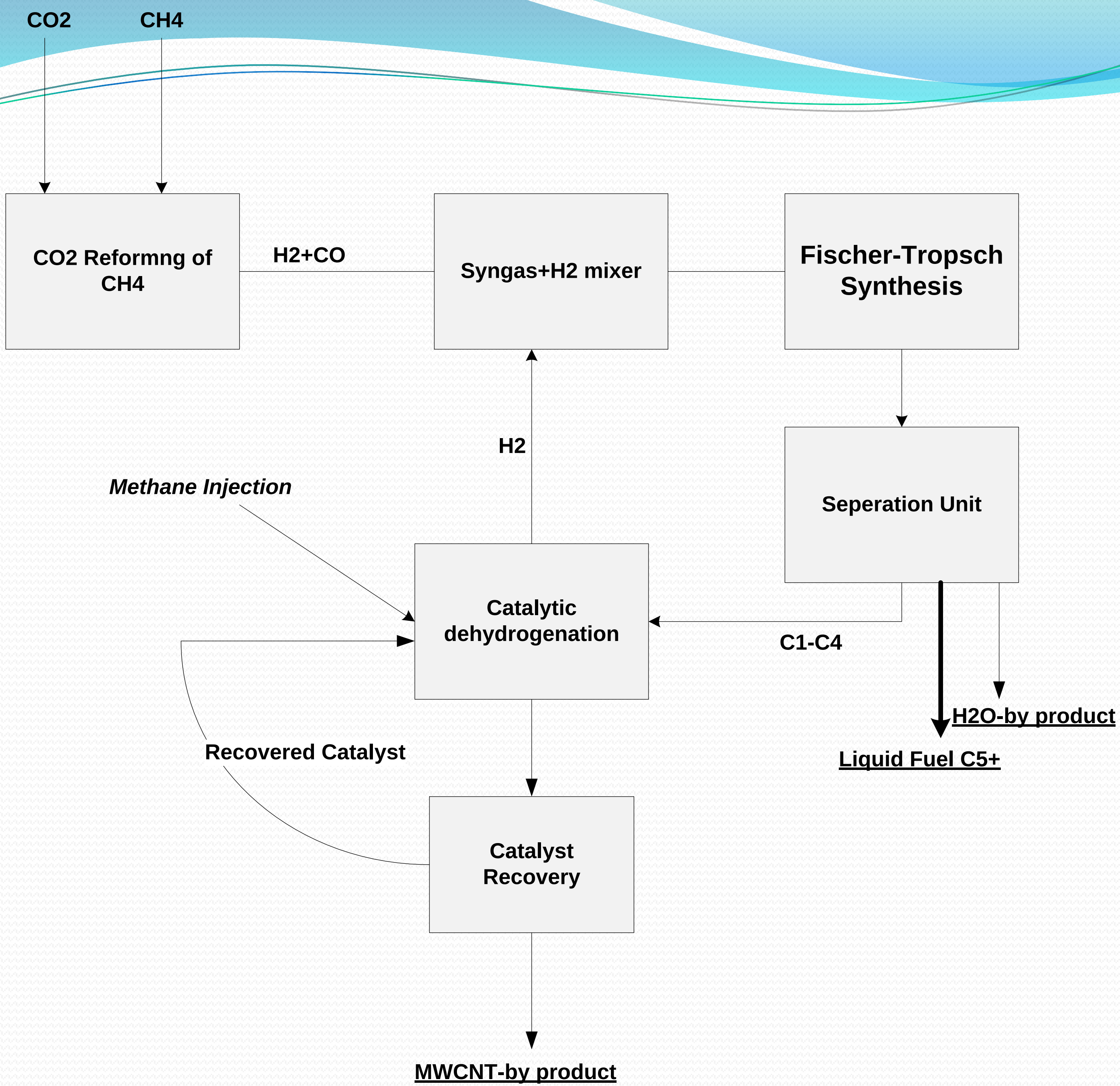
Adsorption $CO_2 + \sup_{(as)} \Leftrightarrow CO_2 - \sup_{(as)}$

Reaction Surface $M_{(as)} - CH_3 + CO_2 - \sup_{(as)} \Rightarrow 2CO_{(g)} + 2H_2 + M_{(as)} + M_{(as)} + \sup_{(as)}$

Dry Reforming Process Technologies

- *Fluidized*
- *Fixed bed reactors*
- *Nonthermal plasma*
  - Stability of Methane
  - High temperatures and pressures suffer to carbon deposit
- *Membrane Technology*
  - Thermodynamic equilibrium


CH4 + CO2
electrical supply
electrodes
syngas (H2 + CO)


CO2
CH4
CO2 Reformng of CH4
H2+CO
Syngas+H2 mixer
Fischer-Tropsch Synthesis
H2
Methane Injection
Seperation Unit
Catalytic dehydrogenation
C1-C4
H2O-by product
Liquid Fuel C5+
Recovered Catalyst
Catalyst Recovery
MWCNT-by product

Fischer-Tropsch Synthesis

Fischer-Tropsch synthesis

♥

in GTL process

Fischer Tropsch Reaction

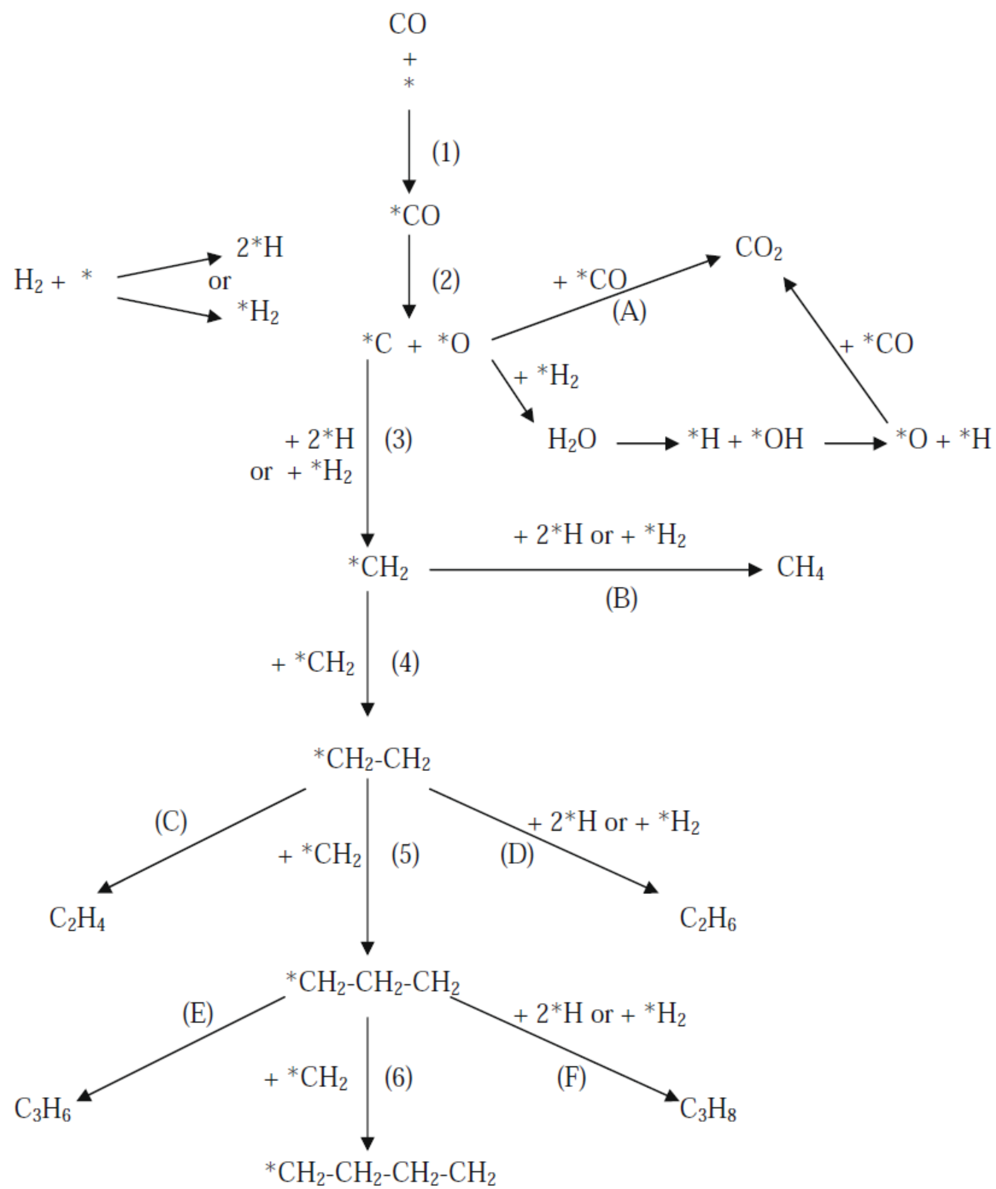
- Fischer-Tropsch reaction

$$CO + 2H_2 \rightarrow -CH_2- + H_2O$$

- Water Gas Shift Reaction

$$CO + H_2O \leftrightarrow H_2 + CO_2$$

Fischer-Tropsch mechanism



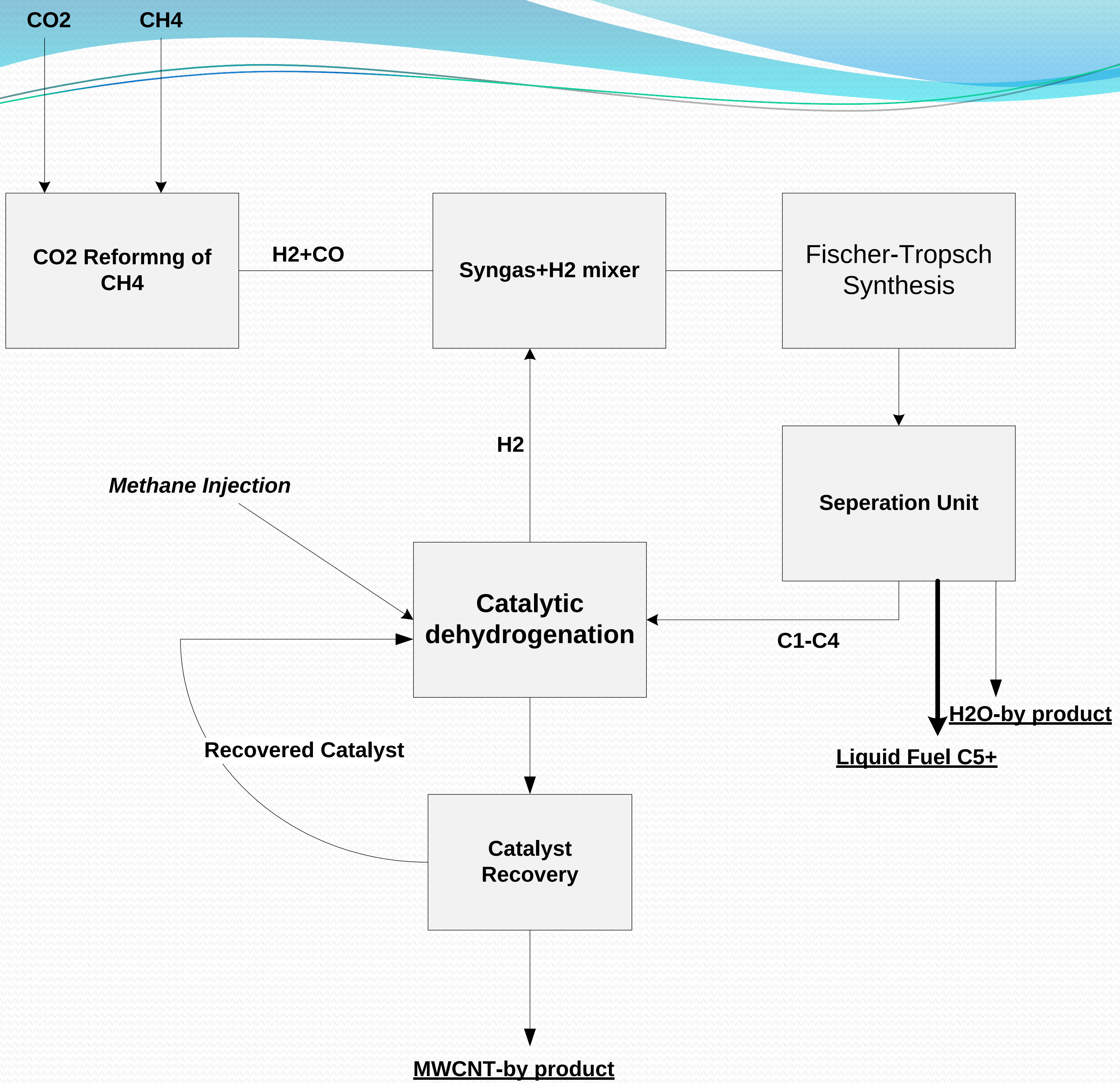
Classification of FT processes

- Low-Temperature Fischer-Tropsch:
  - ✓ 220°C to 250°C
    - ✓ multi-tubular packed bed
      - ✓ Iron-based, Co-based catalyst
        - ✓ long chain molecules

- ✓ High-Temperature Fischer-Tropsch
  - ✓ Above 300°C
    - ✓ fixed fluidized bed reactors
      - ✓ Iron-based catalyst
        - ✓ lighter product slate

Products of Fischer-Tropsch Synthesis

- HTFT product spectrum much lighter than that of the two LTFT processes
- Iron-FT catalysts much more oxygenates than cobalt-FT catalysts
- Iron-FT catalysts much more olefinic product spectrum than cobalt catalysts
    - Fe-HTFT synthesis: gasoline and light olefins
    - Two LTFT processes: middle distillates


CO2
CH4
CO2 Reformng of CH4
H2+CO
Syngas+H2 mixer
Fischer-Tropsch Synthesis
H2
Methane Injection
Seperation Unit
Catalytic dehydrogenation
C1-C4
H2O-by product
Liquid Fuel C5+
Recovered Catalyst
Catalyst Recovery
MWCNT-by product

Catalytic dehydrogenation

- Low H_2/CO ratios:0.7–1.1 in DRM

- Water–gas shift (WGS) in FTS technology to raise the hydrogen content of the syngas to the required levels

$$CO + H_2O \rightarrow H_2 + CO_2$$

  - one CO_2 molecule for each H_2 molecule in WGS reaction

- Catalytic dehydrogenation (CDH) of the (C_1–C_4) products of the Fischer–Tropsch synthesis (FTS)

Catalytic Dehydrogenation

- CDH reaction in a state of psuedo-equilibrium:

$$CH_4 \leftrightarrow \left[CH_4^+\right] \rightarrow C_M + 2H_2$$

At a given temperature as the bonds of the activated complex break to form:

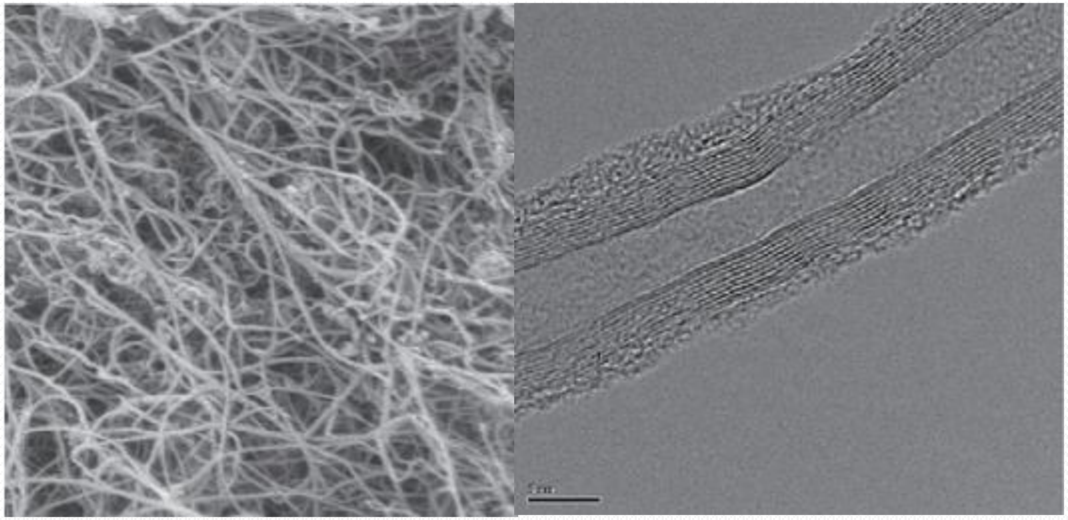
- H2
- Solid carbon in the form of MWCNT (C_M)

Catalyst and production

Nano-scale

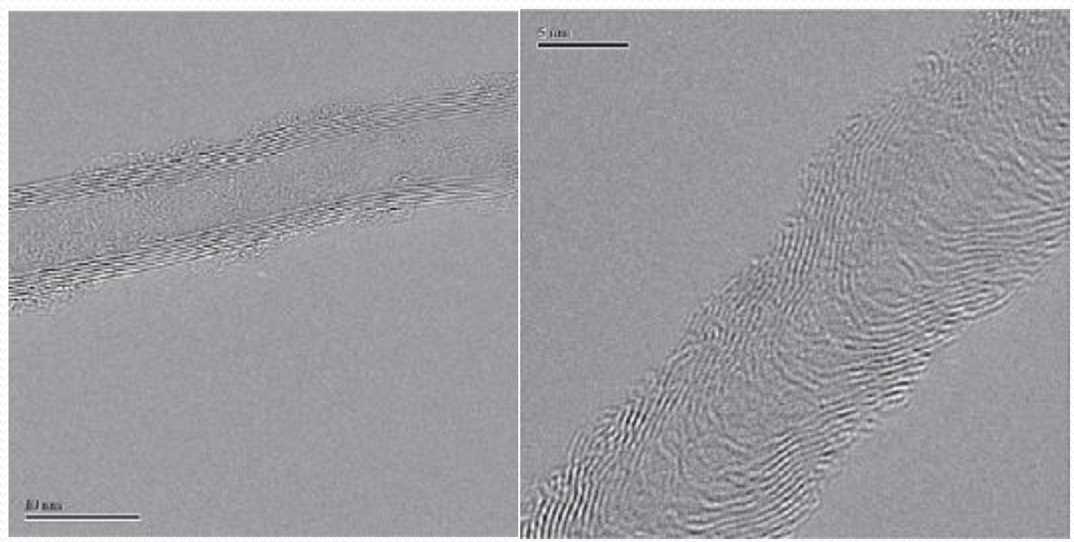
Fe–M (M = Pd, Mo or Ni) catalysts supported on Alumina

- Decomposition of lower alkanes to produce hydrogen
- Carbon nanofibers or nanotubes
  - Above 600 °C, multi-walled nanotubes with parallel walls in the form of concentric graphene sheets.
  - At or below 500 °C, carbon nanofibers with capped



MWCNT @ 700 C
(CDH of methae)

Fig 5. Typical CNT production in CDH process [Hofman 2011]



SCNT @ 500 C
(CDH of propane)

CO_2 emissions avoided, water saved and products

- methane injected into the CDH reactor : ΔC_1
- gaseous products for a FTS-CDH-MI plant

$$\Delta C_1 + (C_1\text{–}C_4)$$

- Total reactants yielding oil products

$$C_{5+} = 100\% - (\Delta C1 + (C_1\text{–}C4))$$

- Hydrogen product

$$\Delta H_2(wt.\%) = x_1\% \times [C_1] + x_2\% \times [C_2 - C_4]_{par} + x_3\% \times [C_2 - C_4]ol$$

- MNT product

$$\Delta C_{MNT}(wt.\%) = (100 - x_1)\% \times [C_1] + (100 - x_2)\% \times [C_2 - C_4]_{par} + (100 - x_3)\% \times [C_2 - C_4]_{ol}$$

- Typical catalyst in FTS with α=0.83

$$\Delta H_2(wt.\%) = 25\% \times [C_1] + 20.82\% \times [C_2 - C_4]_{par} + 14.29\% \times [C_2 - C_4]ol$$

$$\Delta C_{MNT}(wt.\%) = 75\% \times [C_1] + 79.18\% \times [C_2 - C_4]_{par} + 85.71\% \times [C_2 - C_4]_{ol}$$

- The weight of Water saved

  $18/2 \times$ the weight of H_2 produced by CDH

- CO_2 emissions avoided

  $44/2 \times$ the weight of H_2 produced

Product and environmental saving

Typical products and environmental savings for a 50,000 barrel/day FTS-CDH-MI plant with a typical catalyst $\alpha = 83$ *

Products	Weight (tons/day)
50,000 barrel of oil	7229
H2	1000
Total CNT	2930
Environmental saving	
CO2 avoided	22007
H2O saved	9002

* according to Gerald P. Huffman research

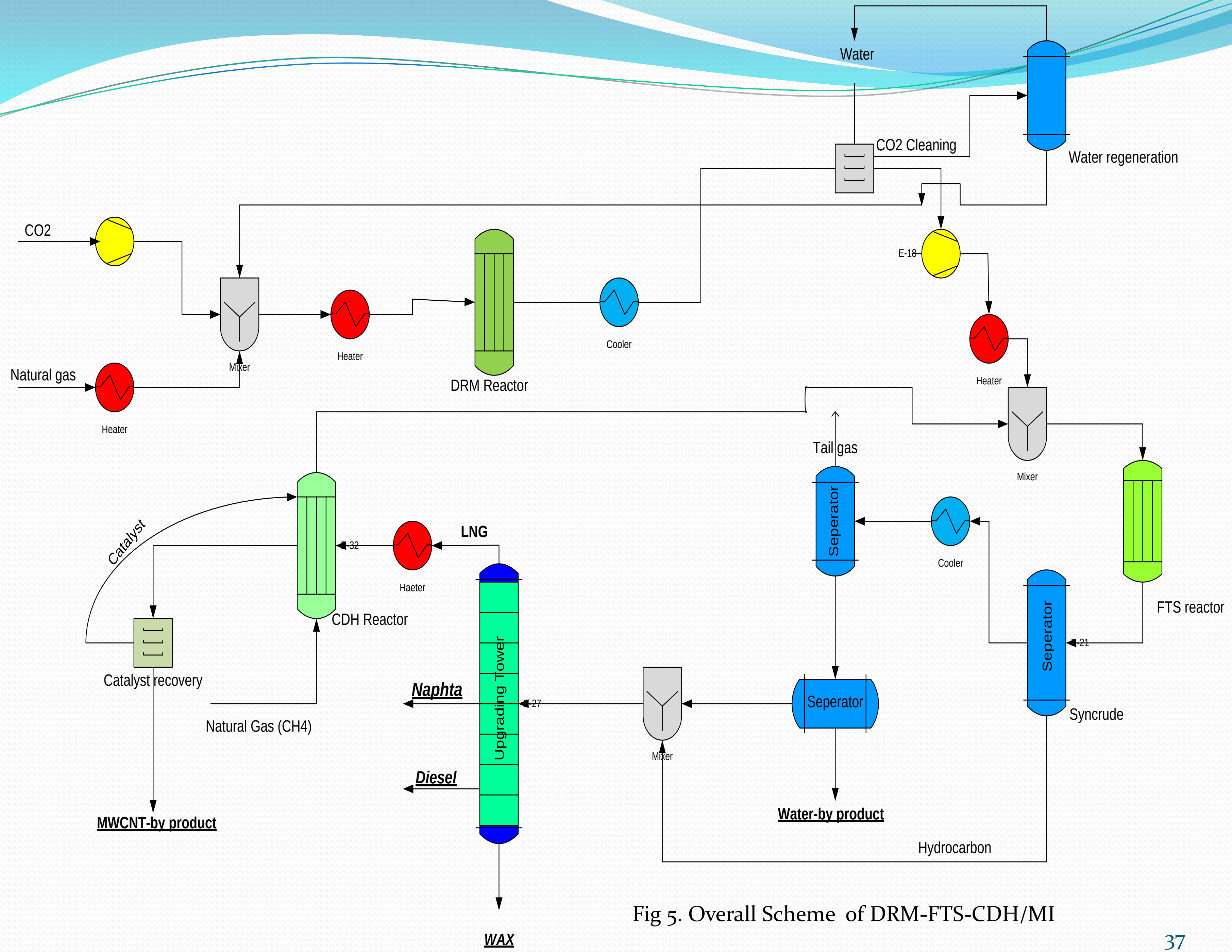


Fig 5. Overall Scheme of DRM-FTS-CDH/MI

conclusion

- DRM-FTS-CDH/MI to avoid CO_2 emission and flare gas recovery
  - The mitigation and utilization of greenhouse gases, such as carbon dioxide and methane
  - High quality oil (C_{5+}) production
  - Reduction of steam and fuel gas consumption
  - Specific values of the H_2/CO ratio for specific products
  - Hydrogen in the product could be applied as a fuel in fuel cells
  - The water saved by avoiding the water-gas shift reaction
  - Production of Multi-walled carbon nanotubes (MWCNT)
- Removal of toxic metals from water
- Ultra-strong MWCNT fibers and ropes for use in transmission lines and cables
- Replacement of carbon black in tires by MWCNT to improve the durability of tires
- Composites for use as structural materials in automobiles and trucks, airplanes, body and vehicle armor, and sports

Thank you for your Attention

- He is Majid Sarkari 29 year-old from Iran. He received his MSc degree in 2011 in the Chemical Engineering, Kinetic and thermodynamic field from Sistan and Baluchestan University of Iran. His research interests are Fischer-Tropsch synthesis, catalytic reaction engineering, ultra fuel production from renewable resources, environmental catalysis. He has published more than 20 papers in international journals and conferences. He currently works at South Pars Gas complex as a process engineer.