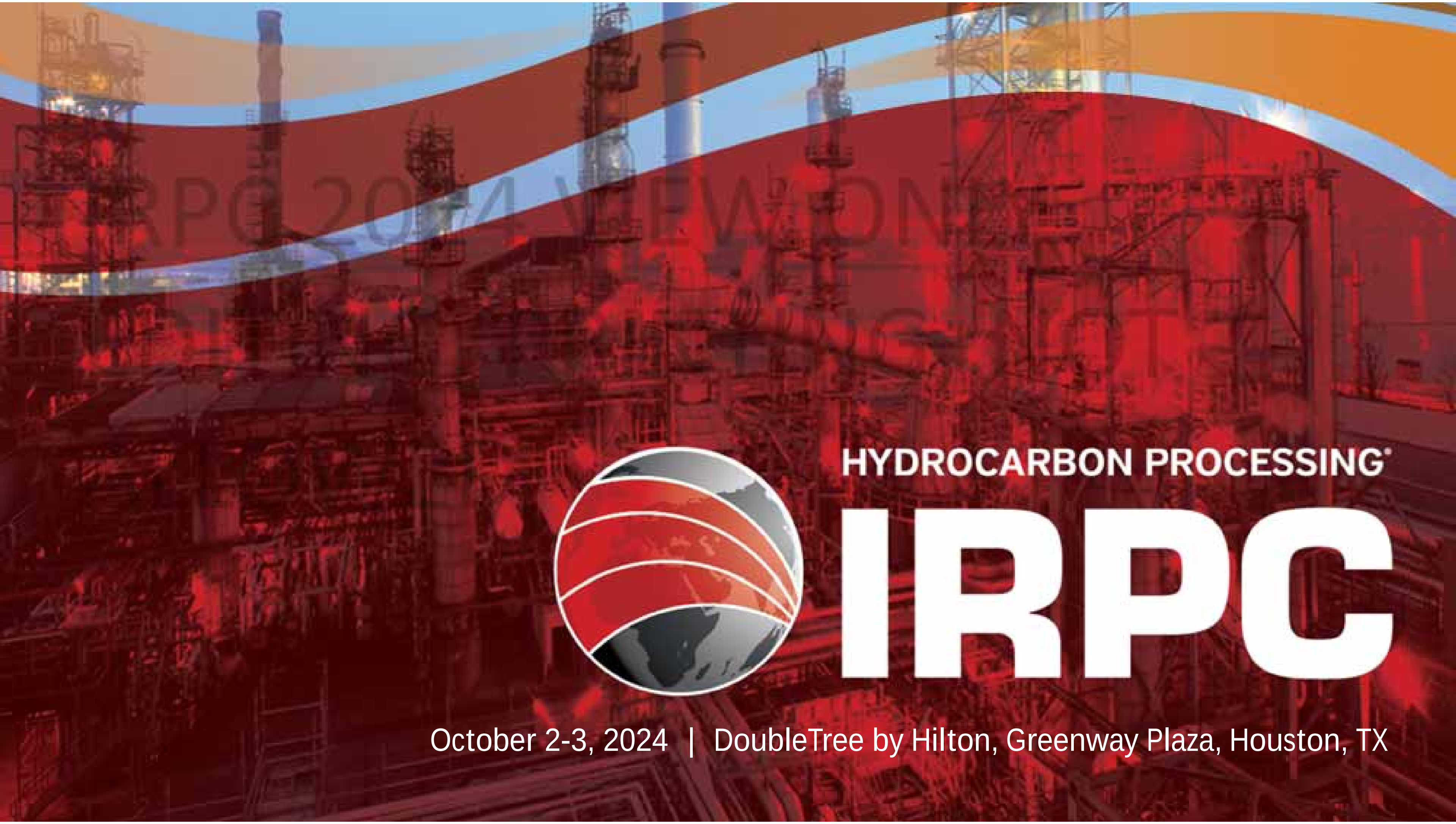
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Off-Gas Treatment to Mitigate Environmental Impact

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OCTOBER 2 , 2024

Off-Gas Treatment to Mitigate Environmental Impact

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Off-gas Treatment To Mitigate Environment Impact

Off-gas in Refineries & Petrochemical Complexes : Major contributor to environmental impact

A typical refinery complex contributing to off-gas emissions.

Courtesy : The lowdown on Blowdown- The Chemical Engineer

Focus on emission abatement and monetization

Off-gas Treatment To Mitigate Environment Impact

Environmental impact

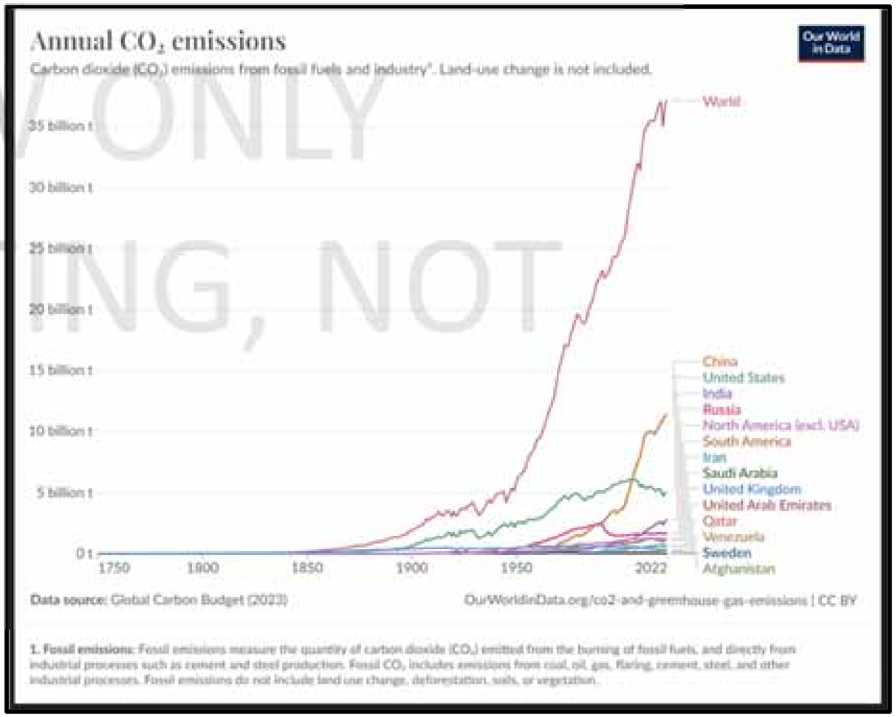
Major contributor CO_2 emissions: Off-gases

Global initiatives

- G20 countries' emission reduction targets
- World Bank's Global Gas Flaring Reduction Partnership (GGFR)
- US EPA's Global Methane Initiative (GMI)

Global carbon emissions in recent years:

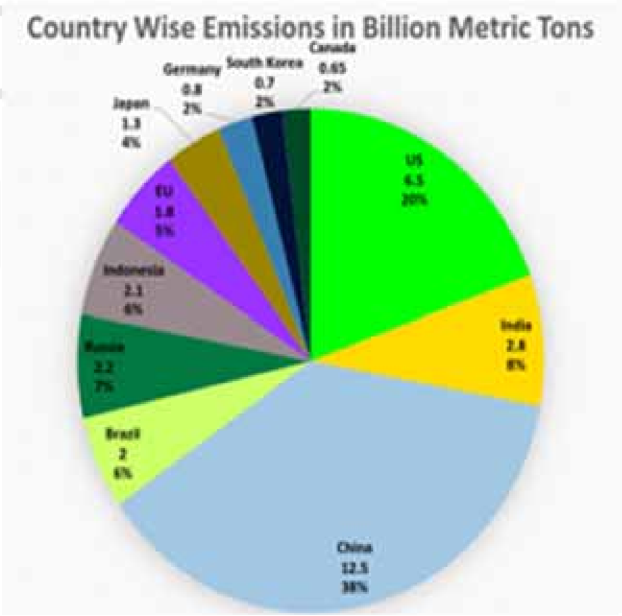
- 2021: 36.8 B MT
- 2022: 34.2 B MT
- 2023: 34.4 B MT
- 2024: > 35 B MT



Off-Gas Abatement Projects

Off-Gas Composition

- Hydrogen
- CO_2 / H_2S: removed with treatment
- C_1: Methane
- C_2: Ethane & Ethylene
- Light ends: C_3's & C_4's (small amounts)



Off-Gas Abatement Projects

Benefits

- Reuse as fuel gas
- Mixed with feed for processing units
- Hydrogen recovery
- Feed for Syncrude, Methanol & valuable chemicals

Off-gas Treatment To Mitigate Environment Impact

Off-Gas Abatement Projects

Hydrogen Recovery
- Light hydrocarbon off-gas streams from processing units
- Hydrogen rich purge gas streams from hydro-processing units

Hydrocarbon Recovery
- Components: Methane, ethane, ethylene

Flare Gas Recovery
- Hydrocarbon reliefs from upstream & downstream processing units

Production of Synthetic Crude
- Conversion of off-gases to CO & H_2.

Off-Gas Abatement Projects - Upstream

Hydrogen Recovery Methods

- PSA systems
- Membrane-based separators
- Combined Membrane and PSA Process
- Cryogenic separation

Off-Gas Abatement Projects

Monetization Methods

- Partial Oxidation
- Methane / Ethane Pyrolysis
- Fischer-Tropsch Processes
- Flare Gas recovery
- GTL Process
- Hydrogen as fuel
- LOOP Process
- BrightLoop Technology

Pressure Swing Adsorption (PSA) System

System: multibed adsorption system with shape-selective zeolites.
Function: holds separate molecules based on their molecular size.
Recovery Rate: 85% of the feed hydrogen or higher.
Bed Saturation: beds are saturated with H_2 molecules.
Depressurization: PSA beds are depressurized to evacuate held-up molecules.

Multiple Vessels ensure steady availability of hydrogen alternating between depressurization and operation modes.

Membrane Process

Selective Permeability: Hydrogen molecules are smaller.
Motive Force: High differential pressure across membrane.
Separation: Permeate side collects H_2, retentate side contains remaining gases.

Challenges: Membrane fouling over time.
Purity Limitation: A single membrane may not achieve the highest purity levels.

Combined Membrane and PSA Process

Purity Level: A single membrane cannot achieve purity level.
Membrane Stage: Initial separation to enrich H_2 content.
PSA Addition: Further purification to achieve 99.9% purity.
Usage: Suitable for high pressure off gases.
Efficiency: 90% recovery or higher.

Cost: More expensive than a PSA-only option.

Cryogenic Process

Process: Utilizes low temperature distillation & PSA.
Separation: Desorbed tail gas compressed & cryogenically distilled.
Recovery: Purified gases are fed back to PSA.
Purity Level: 99.9% hydrogen purity level.
Efficiency: Recover up to 95% or higher hydrogen.
Cost: Highly expensive; more equipment count; high CAPEX & OPEX.

Off-gas Treatment To Mitigate Environment Impact

Membrane, PSA & Cryogenic Process comparis

Features	PSA	Membranes + PSA	Cryogenics
H_2 Purity	99.9%+	90-98%	90-96%
H_2 recovery	75-92%	85-95%	90-98%
Feed Pressure	Medium	High	Low
Feed H_2 Content	>40%	>25%	> 10%
H_2 Product Pressure	Feed pressure	< Feed pressure	Feed /low pressure
H_2 Capacity	>85 % recovery	Higher recovery	Highest recovery
Equipment Count	Multiple PSA beds	Membranes + PSA + compressors.	Cold boxes + PSA + compressors.
Capital Cost	Low	Medium	Higher

Methane / Ethane Pyrolysis

Reaction: Heating methane to high temperatures in absence of oxygen.

$$CH_4 \rightarrow C + 2H_4$$

Methane Pyrolysis

Conditions: High temperatures >1000°C to ensure efficient decomposition.

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Ethane Pyrolysis

CO_2 Free Hydrogen Production: used in fuel cells, refining processes, clean energy source.

Carbon Products: Solid carbon byproduct has applications in industries like rubber manufacturing, electronics, and energy storage.

Partial Oxidation (POx)

Reaction: Hydrocarbons react with a limited amount of oxygen.

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$$

Conditions: High temperatures ~1000°C & with /without catalyst

Hydrogen Production: Refining processes, a clean energy source.

Syngas Production: for methanol, NH_3, Synthetic fuels via Fischer-Tropsch synthesis.

Air Products offers proprietary POx based Blue H_2 Solution (POx) is a proven commercial process capable to process refinery off-gas

Off-gas Treatment To Mitigate Environment Impact

Compare Partial Oxidation & Methane Pyrolysis

Partial Oxidation (Advantages)

- Catalyst-Free Option : Non-catalytic POx avoids issues catalyst cost, poisoning, and coking
- Energy Efficiency : heat internally, used to drive the reaction, improving overall energy efficiency.

Challenges

- Soot Formation: Controlling the reaction to minimize soot and by-products is essential.

Methane Pyrolysis (Advantages)

- CO_2-Free Hydrogen: Unlike Methane reforming, methane pyrolysis does not produce CO_2, a cleaner method.
- Solid Carbon Byproduct: Good carbon quality used to make carbon black, carbon fibers, and other carbon materials.

Challenges

- Energy Intensive: Significant energy required to maintain high temperatures for methane decomposition.

LOOP Process (UK company “Levidian”, Plasma technology)

Process: Uses a low-temperature, low-pressure process to crack methane into hydrogen and carbon without catalysts or additives.

Products: Carbon is locked into graphene, and hydrogen can be used as a hydrogen-rich blend or stored in its pure form.

Environmental Impact: CO_2 Reduction: A single LOOP50 device using waste gas reduces CO_2 equivalent (CO_2e) by 100 tons per year.

Levidian partnered with Abu Dhabi’s Zero Carbon company. 10-year contract to deploy 500+ LOOP decarbonization systems in the UAE, removing half a million tons of CO_2.

Off-gas Treatment To Mitigate Environment Impact

BrightLoop Technology (Babcock & Wilcox (B&W))

Feedstocks: Gaseous fuels / off-gas to produce H_2 and isolate CO_2.

Process: Chemical Looping based on oxidation and reduction of a Proprietary oxygen carrier particle.

Carbon Capture: High rate of CO2 isolation, no expensive methods.

Products: Predominantly CO_2 & H_2, with ability to produce steam or syngas.

Environmental Impact: Contributes to net-zero goals, more environmentally friendly way. DOE-sponsored projects demonstrated continuous low-carbon hydrogen generation.

Cost Efficiency: Produces low-carbon hydrogen at competitive cost compared to steam methane reforming (SMR) with carbon capture or electrolysis.

Off-gas Treatment To Mitigate Environment Impact

Synthetic Fuel from captured CO_2 and H_2

Technology: Alternative to sequestration; consumes CO_2 from stack gas or atmosphere.

Hydrogen Source: Hydrogen can be from electrolysis or thermo-chemical splitting.

Credit: $30 credit per ton of CO_2 removed from exhaust stack of fossil-power plants.

Reactions:

- Reverse Water Gas Shift Reaction
- Fischer-Tropsch Reaction to produce Synfuels

Environmental Impact: CO_2 Reduction. **Future Penalty:** Utilities may be facing penalty (estimated: $30 per ton) if CO_2 is not captured and sequestered.

Synfuel Hydrogen Economy: Synfuel economy can be a bridge to a true hydrogen economy.

Off-gas Treatment To Mitigate Environment Impact

Reduced Gas flaring

Flaring processes:

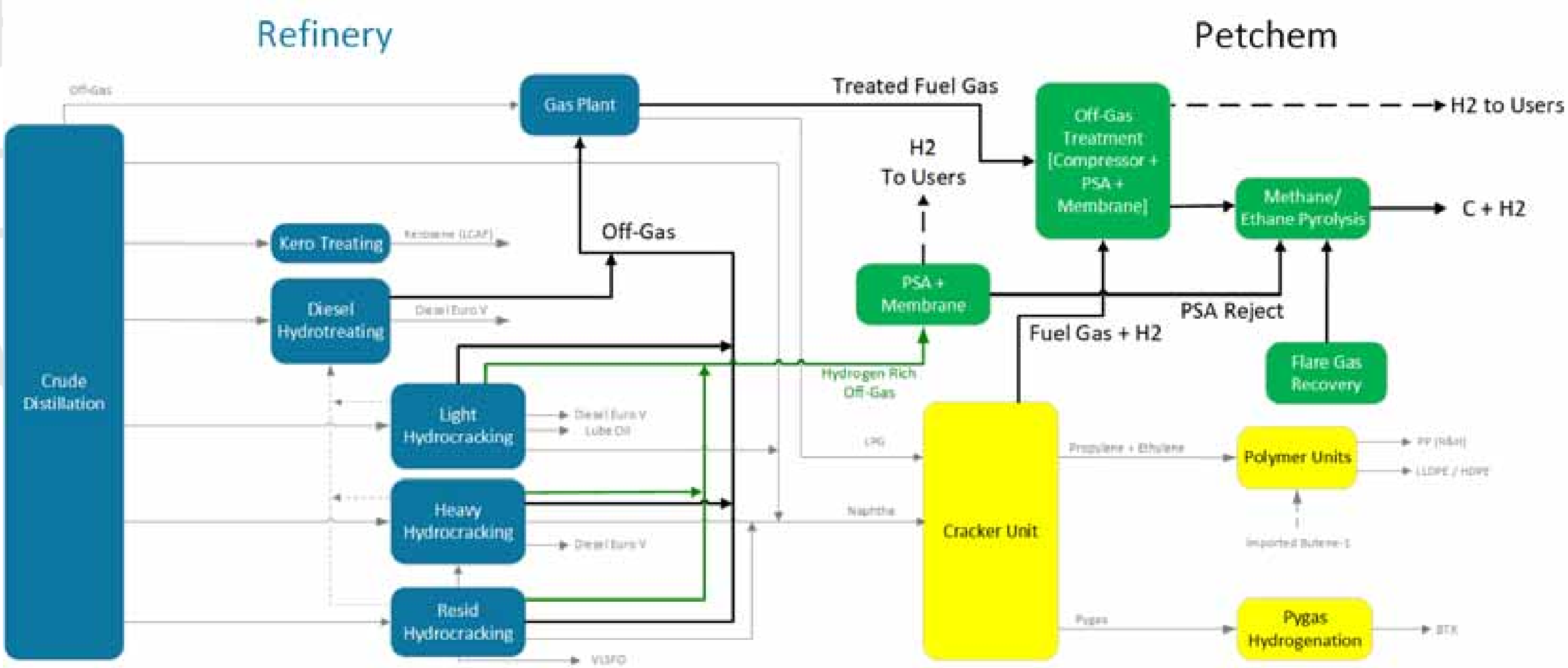
- Emergency flaring, Process / operational flaring, Production flaring

Technical challenges:

- Variable flow rates and compositions
- Low heating value
- Low pressure
- Contains levels of H_2S, CO_2, and other acid gases

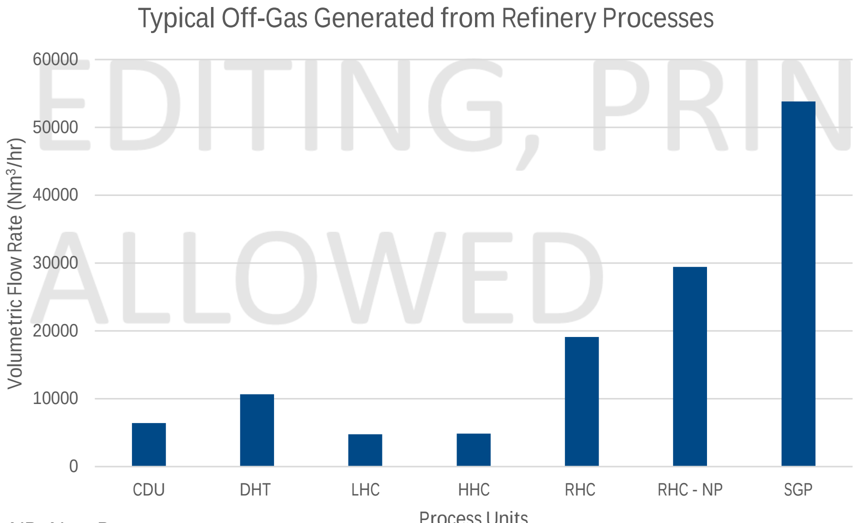
Off-gas Treatment To Mitigate Environment Impact

CASE STUDY 1 : Off-Gas Generated in a Typical Refinery + Petrochemical

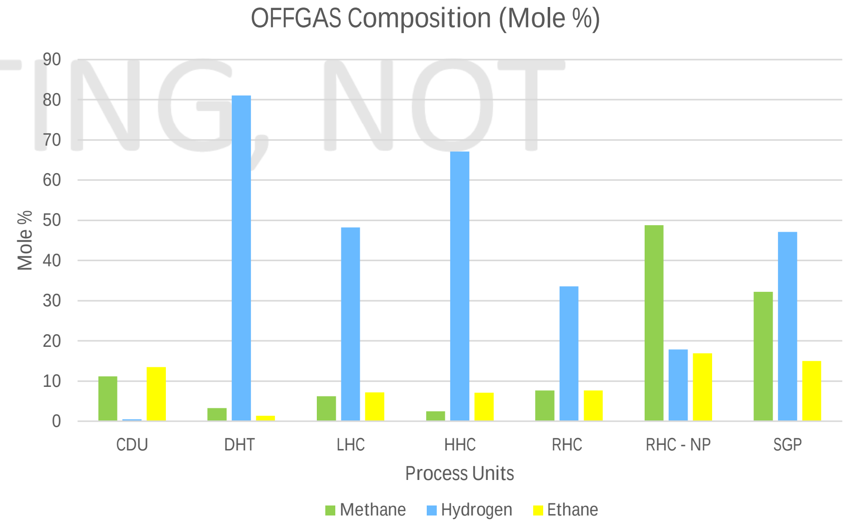


Off-gas Treatment To Mitigate Environment Impact

Off-Gas Volume & Composition (Typical) from the Downstream Process Units

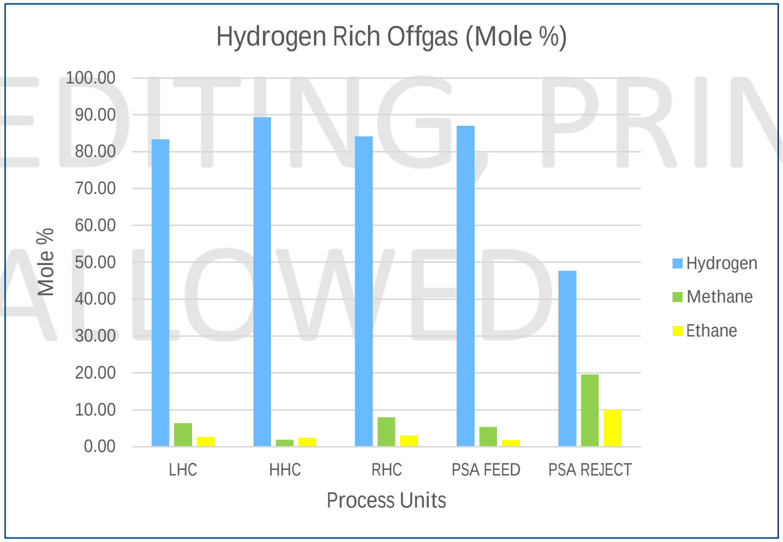


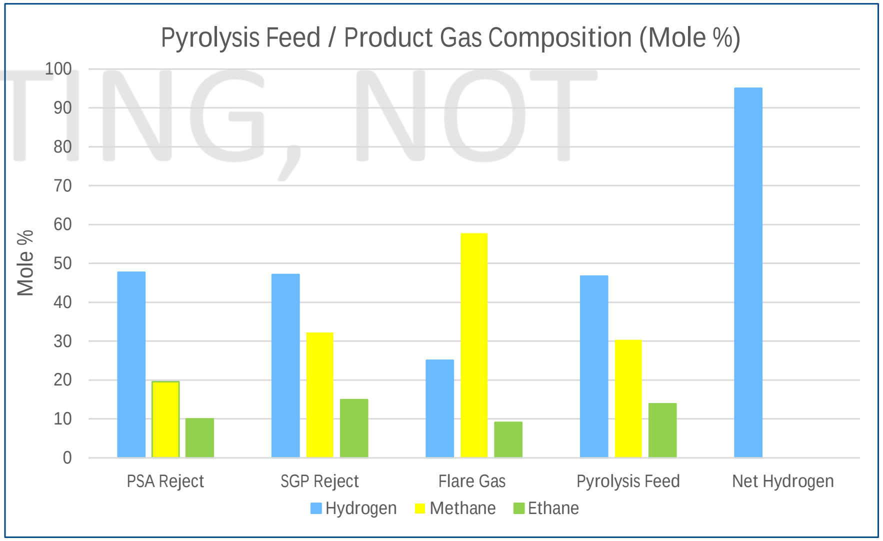
NP: Non-Permeate



Off-gas Treatment To Mitigate Environment Impact

Hydrogen Rich Off-Gas Composition (Typical)





Off-gas Treatment To Mitigate Environment Impact

REFINERY COMPLEX FUEL BALANCE (TYPICAL)

- **FUEL GAS BALANCE**
  - SGP treated gas is blended in fuel gas network.
  - Fuel in furnaces.
  - Hydrogen vented to maintain header pressure.
  - Sales gas demand is 89 tons/hr.

- **OFFGAS ABATEMENT**
  - H_2 recovery in PSA / Membranes
  - PSA off-gases are further processed
  - Option Pyrolysis / Partial Oxidation
  - Methane / Ethane gets converted to H_2
  - Recovered H_2 is blended as fuel

Fuel Gas Balance - Normal Case		
Process Units	**FG Demand**	**FG Supply**
	Tons/hr	Tons/hr
Hydrogen Vent	-	0.6
CDU	18.7	-
SGP	-	32.1
LPG	-	-
DHT	1.8	-
HHC	4.5	-
LHC	3.1	-
RHC	6.1	-
MFC	20.0	-
Utility	34.1	0.7
TOTAL	**88.4**	**33.4**
Makeup Sales Gas	**89**	**33.4**
	1064	**MW**
Sales Gas (Natural Gas) Properties		
LHV	kJ/kg	42,984
MW	g/mol	17.32

Off-gas Treatment To Mitigate Environment Impact

REDUCTION IN NATURAL GAS FIRING

Hydrogen Recovery

- Methane gets converted to hydrogen.
- Ethane gets converted to ethylene & hydrogen.
- Total hydrogen recovered: 7.4 tons/hr.
- Hydrogen can be blended as fuel.
- Reduction in natural gas firing: 21 tons/hr.
- Burners in furnaces are still compatible

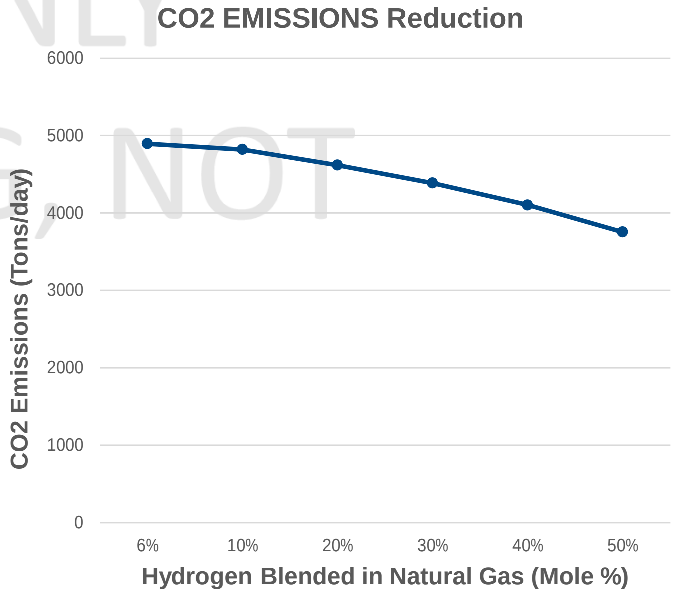
- Reduction in CO_2 emissions:
  57 tons/hr ~1370 Tons/day.

Hydrogen Recovery			
	H2 Recovery Tons/hr	**NG Less Firing** Tons/hr	**CO2 Reduced** Tons/Day
H2 Rich PSA Reject	1.1	3.2	211
SGP PSA Reject	6.1	17	1130
Flare Gas Recovery	0.2	0.4	29
Total	**7.4**	**21**	**1370**

REDUCTION IN NATURAL GAS FIRING

(GREEN OR BLUE) H_2 is blended as fuel

Hydrogen Blending	Natural Gas firing	NG Reduced	CO2 Produced	CO2 Reduced
Kg/hr	Kg/hr	Tons/day	Tons/day	Tons/day
6%	74,209	-	4,898	**-**
10%	73,033	28	4,820	**78**
20%	69,959	74	4,617	**203**
30%	66,471	84	4,387	**230**
40%	62,153	104	4,102	**285**
50%	56,864	127	3,753	**349**



CASE STUDY 2 : GTL

Gas-to-Oil Ratio of the Oil reservoir	200 scf/Bbl
Gas Production from the well	0.4 MMcsfd
Number of wells	10
Total gas production from 10 wells	4 MMscfd
Gas used internal by Oil processing station	1 MMscfd
Gas to be monetized	3 MMscfd
Mini-GTL installed cost	$14.8 Million
Operation and maintenance cost	$500,000 per year
Catalyst replacement cost	$33,000 per year
Electricity consumption	2 MW
Cost of electricity	$989,000 per year ($58/MW)
Catalyst and electrodes replacement cost	
Total cost	$16.3 Million
Simple pay-back ($50/Bbl)	3.1 years

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