



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

SYNGAS UTILIZATION

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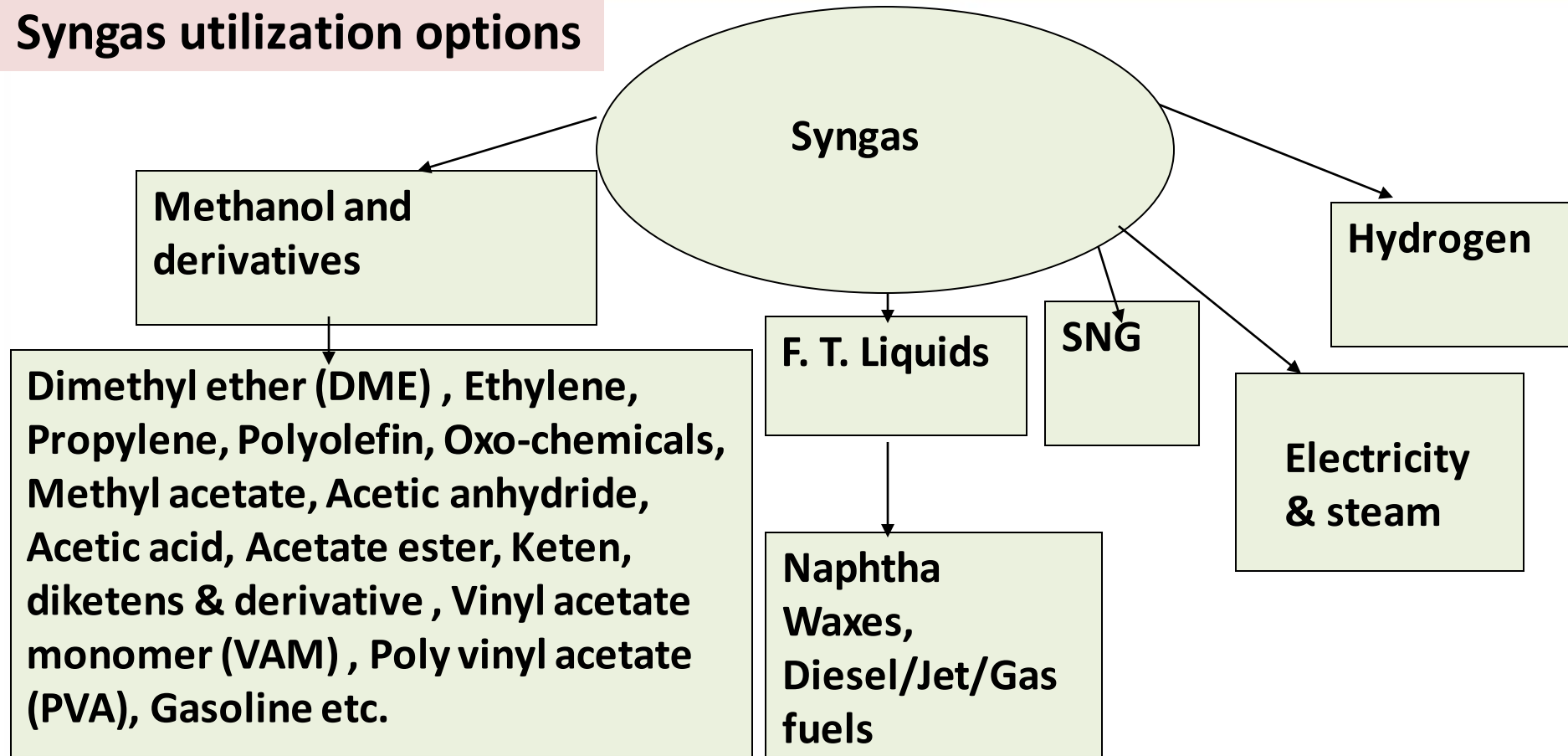


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 - Shift reactions
- Some important utilization
 - F.T synthesis
 - Methanol
 - DME
 - Higher alcohol
 - SNG
 - Hydrogen



Syngas utilization options



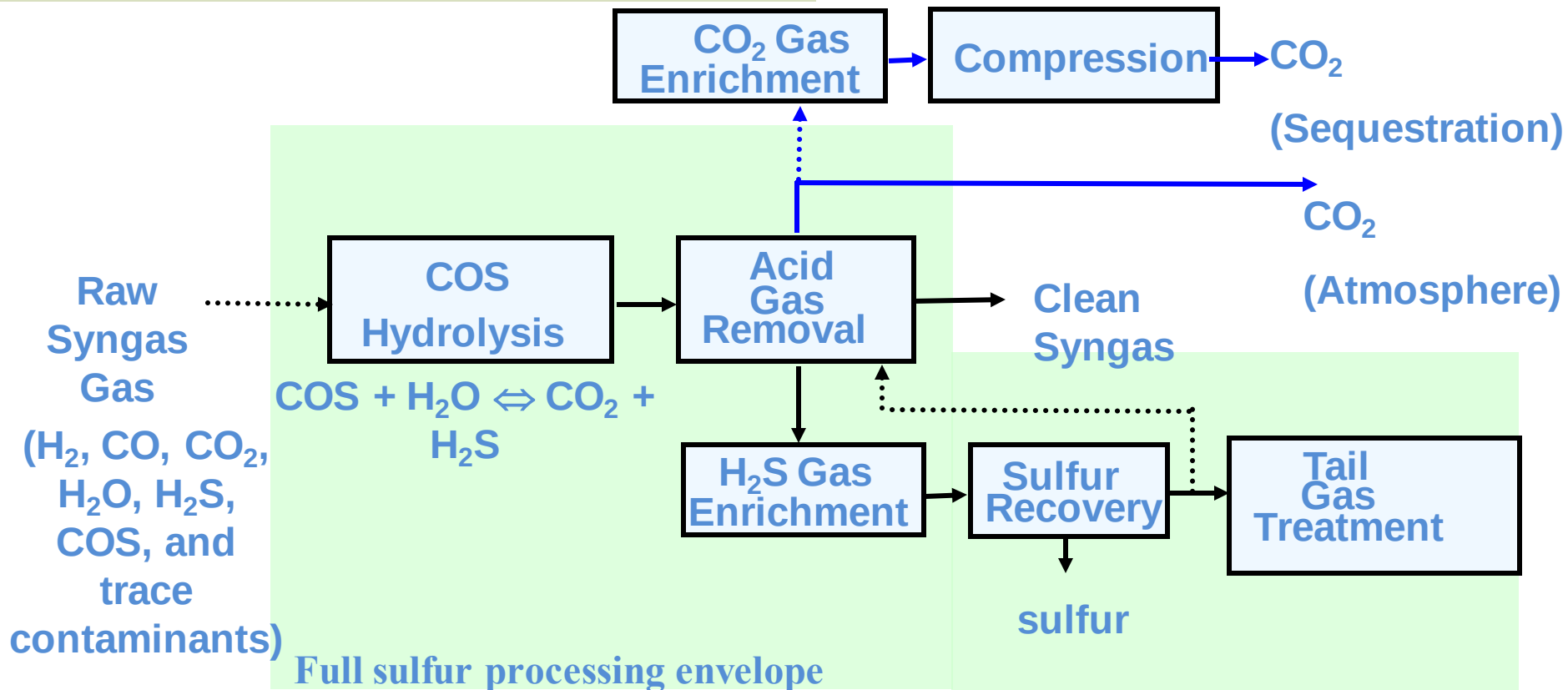
Syngas Cooling and Conditioning

- Reduce syngas temperature
 - Extract valuable energy
 - Use conventional/commercial processes
- Remove chemical species that
 - Foul, corrode, or erode system components
 - Poison or deactivate chemical processing agents
 - Are environmentally unacceptable for release
- Target Syngas purity
 - H_2S and COS concentration
 - CO_2 concentration
- Adjust H_2/CO ratio

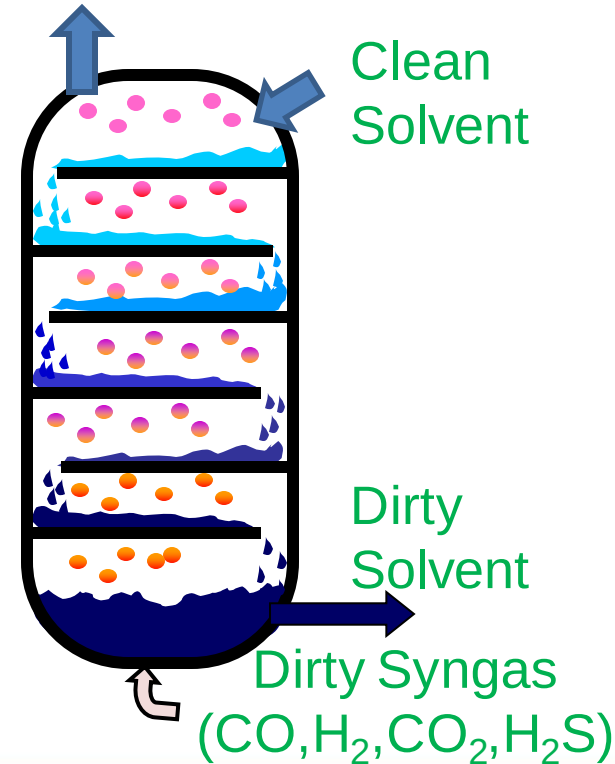


Syngas Cooling and Conditioning

Acid Gas (Sulfur) Processing



Clean Syngas (CO , H_2)



Important Technologies

Solvent absorption based

- MDEA (methyldiethanolamine) -- Chemical absorption
- Selexol tm (primarily dimethyl ethers of polyethylene glycol) -- physical absorption
- Rectisol tm (methanol) -- physical absorption

Adsorption based

- Warm Syngas Cleanup - New technologies (e.g., RTI/Eastman)

Syngas Cooling and Conditioning

Comparison amongst the mostly used absorption methods for acid gas removal

Solvent & Process	Removal (%)	Process parameters	Developed by	Remarks
MDEA (Chemical)	H ₂ S : 98 -99 CO ₂ : ≤ 30	Temp : 30-35 °C (Ambient) Pr :< 2.94 MPa	Union Carbide, UOP, Shell, Dow Chemical,	Lowest capital cost, Moderate operating temp., Only limited physical COS absorption takes place



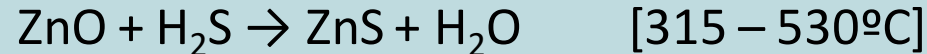
Comparison amongst the mostly used absorption methods for acid gas removal

Solvent & Process	Removal (%)	Process parameters	Developed by	Remarks
Selexol (Physical)	H ₂ S : 99 CO ₂ : Variable	Temp : -7 to- 4 °C Pr : 6.87 MPa	Allied Chemical Corp., Union Carbide, UOP	Higher cost than MDEA but over all system cost including sulfur recovery (SR) process and tail gas treating (TGT) could be more cost effective
Rectisol (Physical)	H ₂ S : 99.5 - 99.9 CO ₂ : 98.5	Temp : -35 to-60 °C Pr : 8.04 MPa	LINDE AG	Highest cost, High selectivity for H ₂ S over CO ₂ , Ability to remove COS

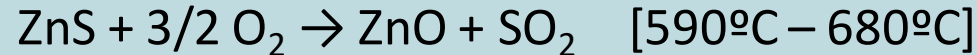
Syngas Cooling and Conditioning

Warm Gas Desulfurization System

- Desulfurization (Adsorber)

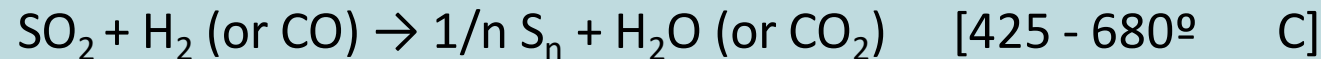


- Regeneration (Regenerator)



- Sulfur Recovery Options

- Claus Process
- Direct Sulfur Recovery Process (DSRP)



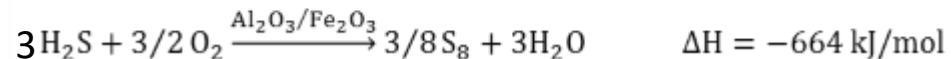
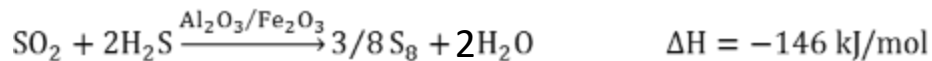
- Sulfuric acid



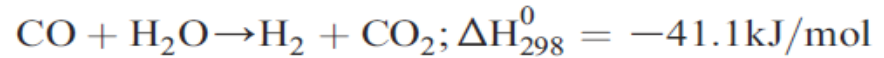
Syngas Cooling and Conditioning

Claus process

Sulfur Recovery Unit (SRU)-Conversion of H_2S in to elemental sulfur



Water Gas Shift Reaction (WGS)



Type of shift reactions

➤ Based on the operating temperature

- HT shift reaction (320-450 °C; $\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$)
- LT shift reaction (200-250 °C; typical catalyst $\text{Cu/ZnO/Al}_2\text{O}_3$)

➤ Based on the position of WGS in flow sheet

- Sweet shift reaction : Takes place after AGR
- Sour shift reaction: Takes place before AGR

• The $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst typically has a relatively higher selectivity than $\text{Fe}_2\text{O}_3\text{--Cr}_2\text{O}_3$, However, it has lower resistance to sulfur and chloride impurities.

• Instead of using separate catalysts in LT/HT shift reactors, catalyst like $\text{Co--Mo/Al}_2\text{O}_3$ can also be used over a wide range of temperatures

❖ Positioning of shift reactor and AGR can influence economy of process and product quality



Characteristics	Sweet shift	Sour shift
Typical Flow sheet	2 (HTS) and 1 (LTS) conversion stages with cooling between the reactors	2 to 3 conversion stages with heat exchangers and sometimes with steam addition as required
CO conversion	Within 2 HTS steps, sweet-gas shift can reduce CO con. from 44.6% to 2.1%. The residual CO can further be converted to 0.5% in LTS step.	From 44.6% to 1.8% within 2 steps using a slightly higher amount of steam. To reach a CO level below 1%, large quantity of steam is added in a third reactor before shift reaction.

Syngas Cooling and Conditioning

Compositional Conditioning

Characteristics	Sweet shift	Sour shift
Catalyst	are usually more expensive	are usually less expensive
Reactor	Size of catalyst bed is smaller.	size of catalyst bed is higher

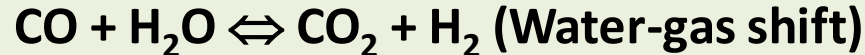
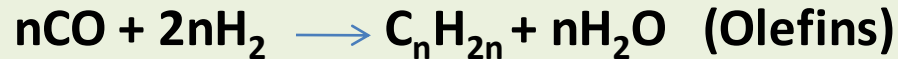
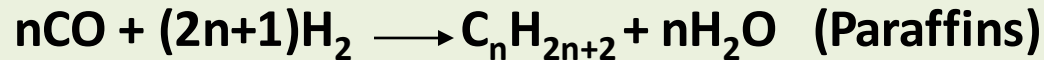
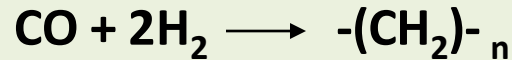
Typical composition of syngas before and after shift reaction S.R

Parameters	H ₂	N ₂	CO	Ar	CH ₄	CO ₂	H ₂ S	COS	H ₂ O	Total
Mole % (before S.R)	43.01	0.35	49.98	0.05	0.39	4.36	1.61	0.08	0.16	100
Mole % (after S.R)	61.53	0.24	1.12	0.03	0.26	35.50	1.14	0.005	0.18	100



Reactions

The syngas is converted to wax, naphtha and diesel, which are followed by upgradation. The wax is hydrocracked to diesel and other products. Main reactions are:

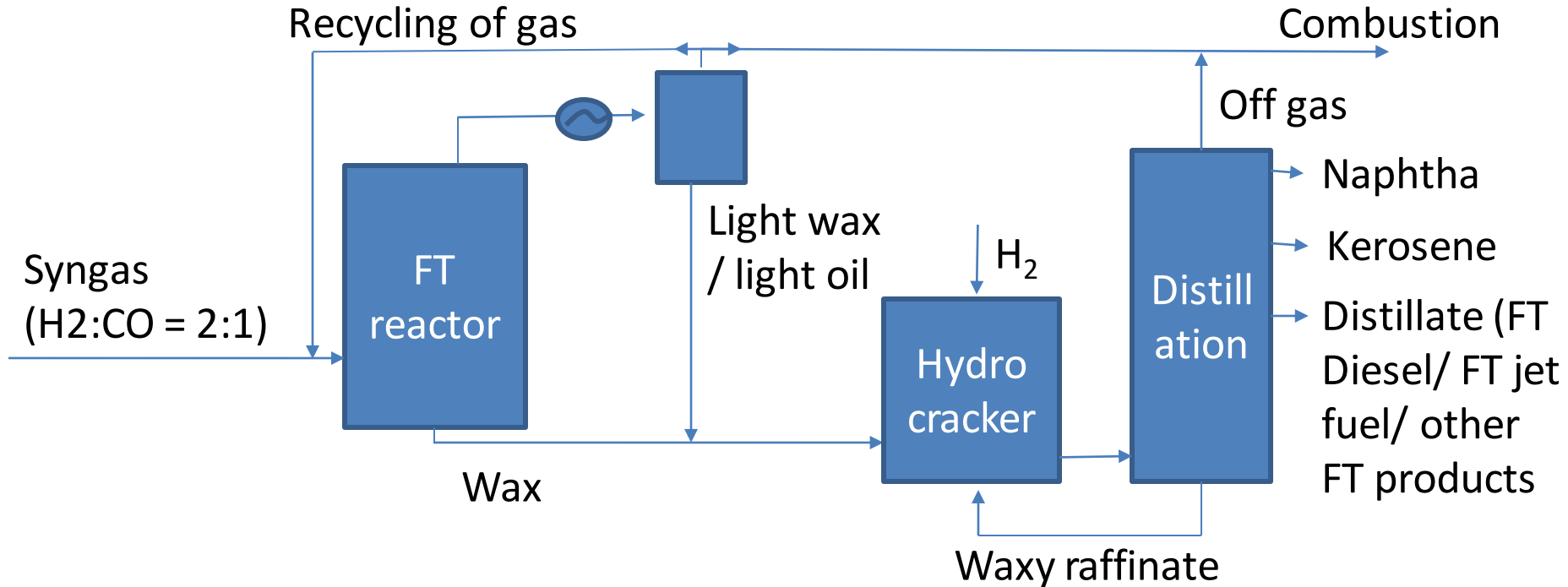


Overall reaction is strongly exothermic

$$(\Delta H = -180 \text{ kJ/mol})$$

Fischer–Tropsch synthesis

Process



Fischer–Tropsch synthesis

Process conditions and catalysts

Operating conditions	Values
H ₂ /CO ratio	2-2.2
Pressure	15-30 bar
Temperature	High temperature 325-370 °C Low temperature 220-27 °C
GHSV	700 h ⁻¹
Catalysts	• Fe based (fuel flexible) • Co based (suitable for high H₂/CO ratio; preferable for natural gas based syngas) • ZSM-5 supported bimetallic FT catalysts for gasoline synthesis

Industrial F-T plant performance data: Fischer-Tropsch synthesis plant may be operated in both high-temperature regime (300-350°C) and low-temperature regime (220-270°C) and with Fe or Co based catalysts.

Typical product distribution

for High Temperature F-T Synthesis

C₅+: 50-80 wt%

Low wax: 4.0 wt%

Gasoline/diesel ratio: 2:1

Cetane number: 50-60

Typical product distribution

for low Temperature F-T Synthesis

C₅+: 20-30 wt%

wax: 50 wt%

Gasoline/diesel ratio: 1:2

Cetane number : 80

Fischer–Tropsch synthesis

Commercial GTL Plants

Plant	Feed for syngas	Capacity	Catalyst	Technology	Year
Sasol Plants (I, II & III), S. Africa	Natural gas	-	-	-	1990
Mossgas Plant, South Africa	-	-	Iron	-	1992
Bintulu Plant, Malaysia	-	12000 bbl/d of kerosene & gasoline	Proprietary catalyst	Shell	1993
GTL Plant at N.W. Australia	-	10000 bpd lube oils and chemical	-	-	-
Pearl GTL Project, Qatar	Natural gas	140000 bbl/d	-	Shell	2006, Project
Sannizaro Refinery, Italy	Natural gas	20 bpd paraffin , upgraded to diesel	Proprietary catalyst	Axens with Eni & ISP, Gase TM Technology	2001-2006



Thanks...

