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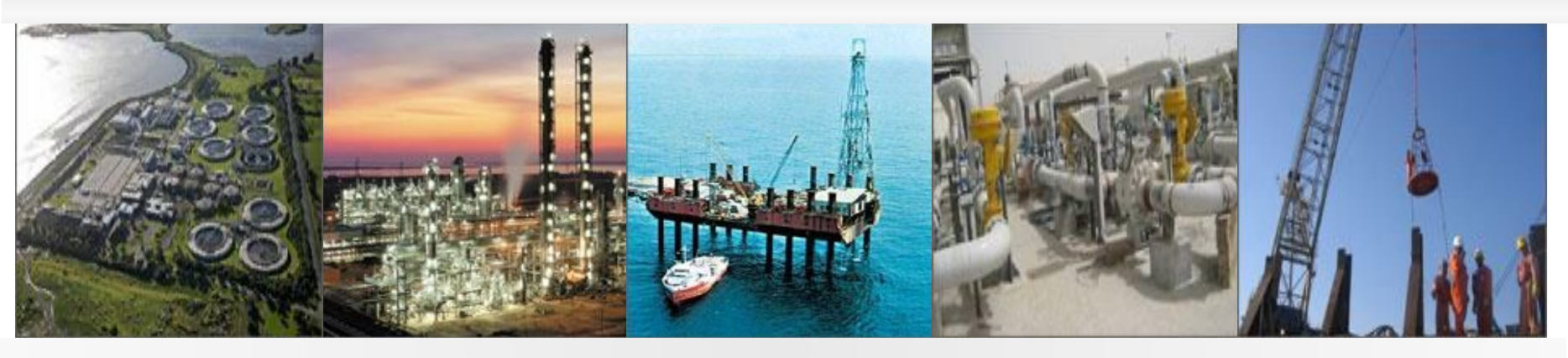


Design Aspects of CTL Process With High Ash Indian Coal: An Efforts Towards Development of CTL Technology

GASIFICATION INDIA 2017, NEW DELHI

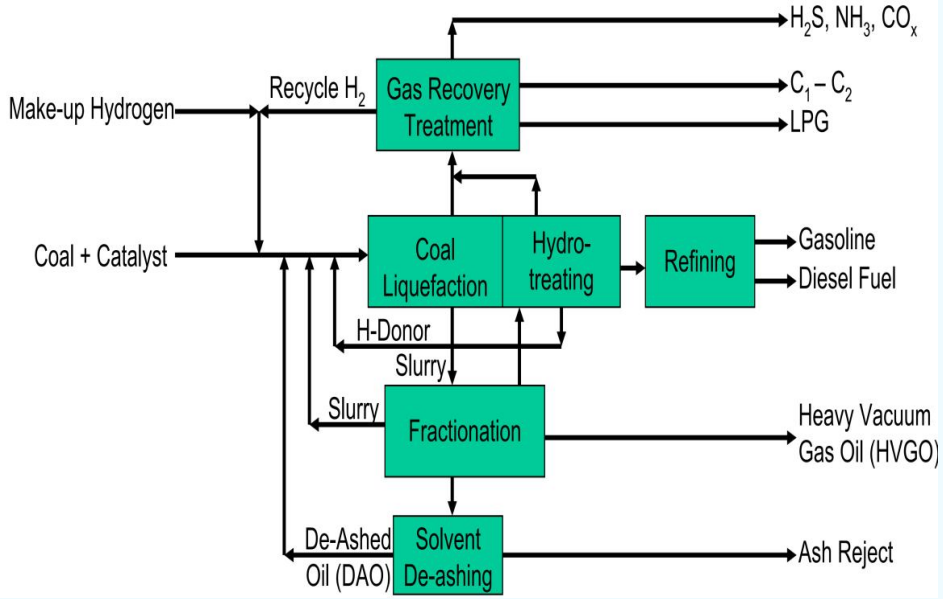
6 - 7 December 2017

Overview of Coal to Liquids

- CTL process: aspects of technology components
- CTL Technology developments efforts
  - Methodology
  - Experimental facilities/pilot plants
  - Demonstration plant
  - Operating results/observations
- Summary

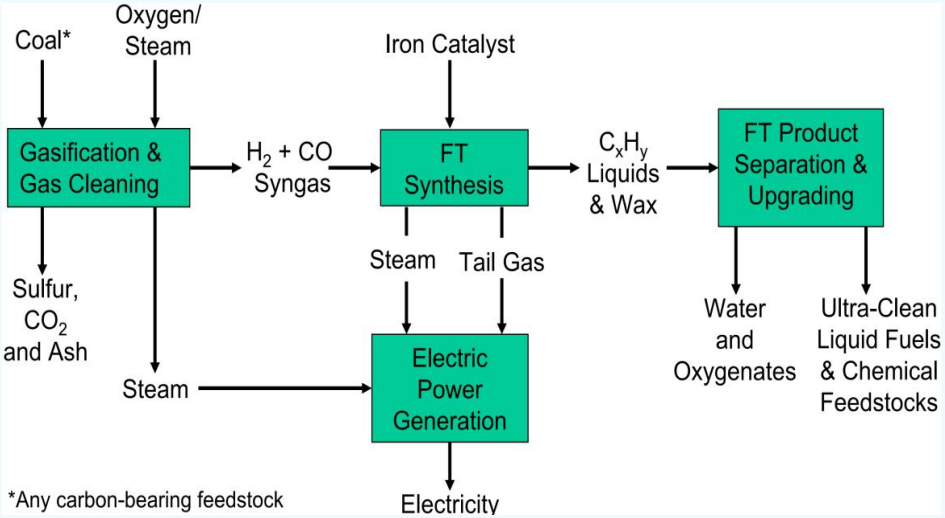
Coal to liquids (Transportation liquids)

Direct coal liquefaction



- **High efficiency potential**
- **No aromatics, high-octane gasoline, low-cetane diesel**
- **Products w/ higher energy density**
- **Water & air emissions issues**
- **Higher operating expenses**
- **Suitable with low ash coal**

Indirect coal liquefaction

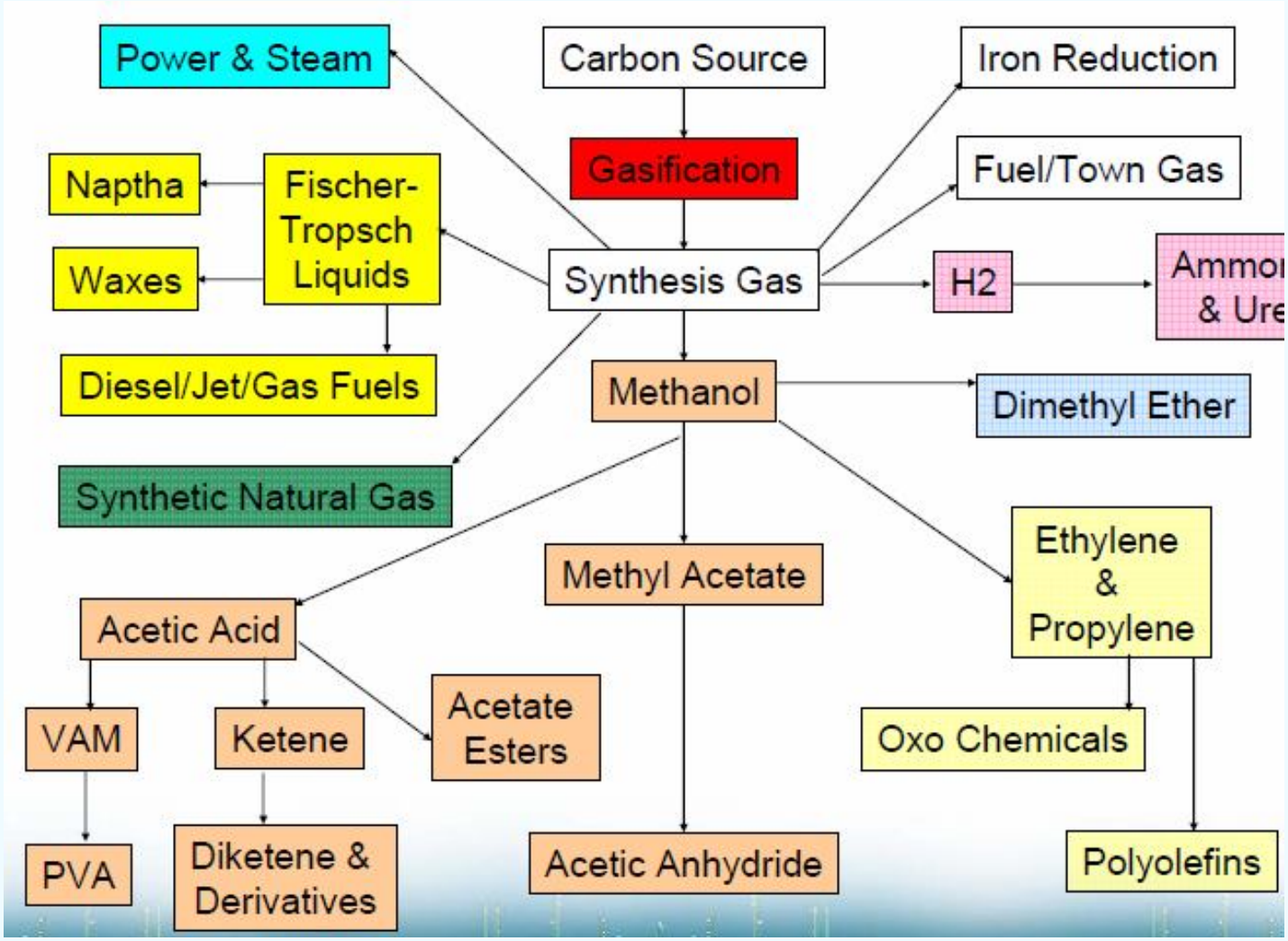


- **Mature & established but complex, less efficient**
- **Low-octane gasoline, ultra-clean diesel**
- **CO_2 capture & power co-production**
- **Use existing refining technologies**
- **Meet all current & projected specifications for sulfur & aromatic**

Incentives of CTL Technology Developments

- Coal is relatively more abundant than oil and gas
- Technologically Feasible
  - Significant advancements made over the years and undergoing major improvements currently
- Economics
  - At present not encouraging but Capital and operating costs – downward trends
  - Expected to be more profitable in the rising prices of oil & gas scenario
- CTL is an umbrella term for a group of technologies
  - Varieties of feeds stock > syngas > polygeneration
  - Energy security/ expanding energy basket

PRODUCT FLEXIBILITY OF SYNGAS



CHEMICALS

Fuels from syngas

- combustion energy content of a product per unit volume is an important economic parameter

Chemicals from syngas

- generally sold by weight for their chemical performance., atom is an important first factor to discriminate between the various chemicals to be produced from syngas

Chemical	CO/H2	Atom selectivity
Methanol	1 / 2	100
Acetic acid	1 / 1	100
Ethylene glycol	2 / 3	100
Acetic anhydride	1 / 1	85
Propionic acid	3 / 4	80
Methacrylic acid	4 / 5	73
Ethanol	1 / 2	72
Acetaldehyde	2 / 3	71
Ethyl acetate	2 / 3	71
Vinyl acetate	4 / 5	70
Ethene	1 / 2	44

REPORTED COMMECIAL USE OF SYNGAS

- Largest - Manufacture of H2, more than half of which is used in the synthesis of ammonia.
- The second largest - in the synthesis of methanol.
- The third largest- conversion to paraffins, olefins and oxygenates via the Fischer-Tropsch reaction.
- The fourth largest- the hydroformylation OXO reaction.

The use of syn gas in the generation of electricity via IGCC has the potential for considerable growth.

CTL through ICL

Four Major Steps

- **Gasification:**
  - Coal preparation, Coal Gasification, Syngas Cooling, Particulate Control
- **Syngas Purification:**
  - Ammonia Scrubbing, Mercury Removal, Acid Gas Removal, CO2 Management
- **FT synthesis:**
  - Catalysts, Reactors (LTFT/HTFT), Water Separations/Product Recovery
- **Product upgradation:**
  - Hydrocracking, Hydrotreating, Isomerisation, etc.

CTL through ICL

Designers interest**:**

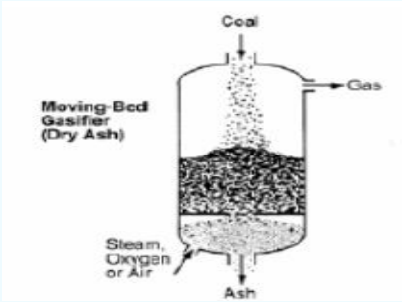
- Throughputs of the different feedstock,
- Optimal conditions for the design feedstock,
- Gas compositions,
- Heat effects,
- Quench requirements
- Startup and shutdown requirements,
- Process control requirements.

Problem due to high ash coals

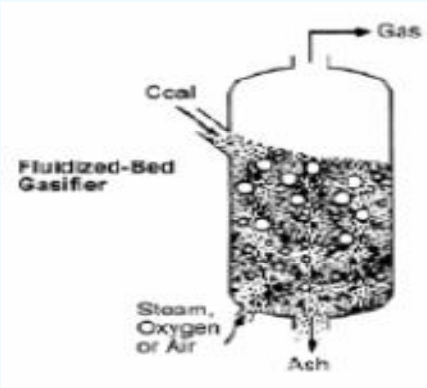
- Erosions of equipment and boiler parts
- Difficulty in pulverization,
- Poor emissivity, poor flame temperature. Low irradiative transfer, more unburnt carbons.
- Excessive amount of fly ash and bottom ash,
- Lower combustion efficiency,
- Increase ash resistivity due to higher amounts of silica and alumina, reduction in ESP efficiency,
- Increased emissions

Gasification

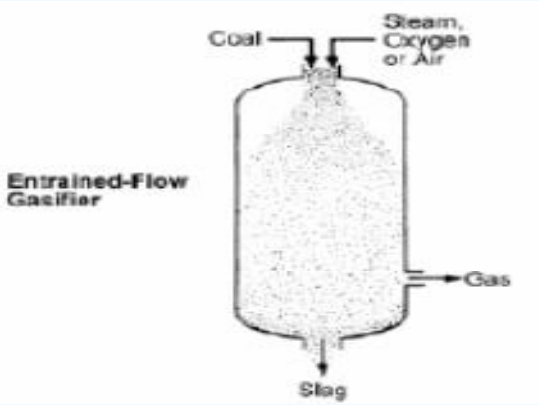
Moving Bed Gasifier:

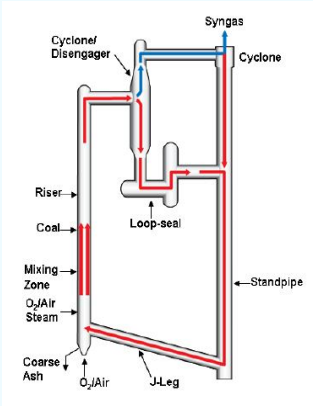


Fluidized Bed Gasifier:



Entrained Flow Bed:





- Indian coals are characterized by
  - High ash content (~ 40%),
  - Low calorific value,
  - Low sulfur,
  - High reactivity and
  - High ash fusion temperature.

- Entrained bed gasification results in loss in efficiency due to inherent high ash content of coal/molten ash penetrations/refratory spoiling.
- Fluidized bed gasifiers are more suitable to Indian coals.

Gasification

Coal
O2/Air
Steam

Exothermic:

- **Partial Combustion of Carbon**
  $C + 0.5O_2 \leftrightarrow CO$; $\Delta H^0_{298} = -110.5$ kJ/mol
- **Complete Combustion of Carbon**
  $C + O_2 \leftrightarrow CO_2$, $\Delta H^0_{298} = -393.5$ kJ/mol
- **Water Gas Shift Reaction**
  $CO + H_2O \leftrightarrow CO_2 + H_2$, $\Delta H^0_{298} = -283.0$ kJ/mol
- **Methanation**
  $C + 2H_2 \leftrightarrow CH_4$
  $\Delta H^0_{298} = -74.5$ kJ/mol
  $CO + 3H_2 \leftrightarrow CH_4 + H_2O$, $\Delta H^0_{298} = -205.8$ kJ/mol

Endothermic:

- **Boudard Reaction**
  $C + CO_2 \leftrightarrow 2CO$, $\Delta H^0_{298} = +172.5$ kJ/mol
- **Steam Reforming Reaction**
  $C + H_2O \leftrightarrow CO + H_2$, $\Delta H^0_{298} = +131.3$ kJ/mol
- **Liberation of Bound Hydrogen**
  $2H \leftrightarrow H_2$, $\Delta H^0_{298} = +431.0$ kJ/mol

Gasifier Gas Composition (Vol %)

H_2	25 - 30
CO	30 - 60
CO_2	5 - 15
H_2O	2 - 30
CH_4	0 – 5
H_2S	0.2 - 1
COS	0 - 0.1
N_2	0.5 - 4
Ar	0.2 - 1
NH_3 + HCN	0 -0.3

Ash/Slag/PM

❑ Key Issues with Gasifiers

- Kinetics (shrinking core?)
- Kinetic/equilibrium controlled?
- Operating P, Temp
- Coal/gas contact
- Syn gas compositions
- Sizing of the gasifier
- Effects of feed variations
- Material of construction
- Engineering Aspects
- Scale-up

Contaminants in Syngas/Allowable Conc

Element	Conc in Coal	Species	Conc in Syngas
S	0.3 – 3.6 wt%	H_2S, COS, CS_2	750-7000 ppmv as H_2S and 25-200 ppmv as COS
N	1.1 – 1.6 wt%	NH_3, HCN	50-800 ppmv as NH_3
Cl	0.003 – 0.37 wt%	HCl, metal chlorides	170-830 ppmv as HCl
Hg	0.02 – 1 µg/g	Hg (g) , $Hg(CH_3)_2$	1.3-63 ppbv
As	0.5 – 80 µg/g	As_2 (g) As_4 (g) , AsH_3 (g) AsS (g)	84-1300 ppbv
Se	0.2 – 1.6 µg/g	H_2Se (g)	32-2600 ppbv
Cd	0.1 – 3 µg/g	Cd (g) , CdS (condensed), $CdCl_2$ (g)	11-340 ppbv

Application	Catalyst/Constraint	S	CO_2	Other Poison
Power	Environmental/Engineering	≤ 40 ppm		
Hydrogen	Cr/Fe; Zn/Cu; Co/Mo	≤ 0.1 ppm		Cl
Ammonia	Ni; Cr/Fe; Zn/Cu	≤ 0.1 ppm	≤ 10 ppm	Cl, Hg, As
SNG	Cr/Fe; Zn/Cu; Ni	≤ 0.1 ppm		Cl, Hg, As
Fischer-Tropsch	Co; Fe	≤ 0.1 ppm		

F-T Synthesis

Synthesis Gas xH_2+yCO → **F-T Reactor (Cat: Co/Fe)** → Syncrude (Long chain aliphatic HC, mainly n-paraffins) $(-CH_2-)_n$

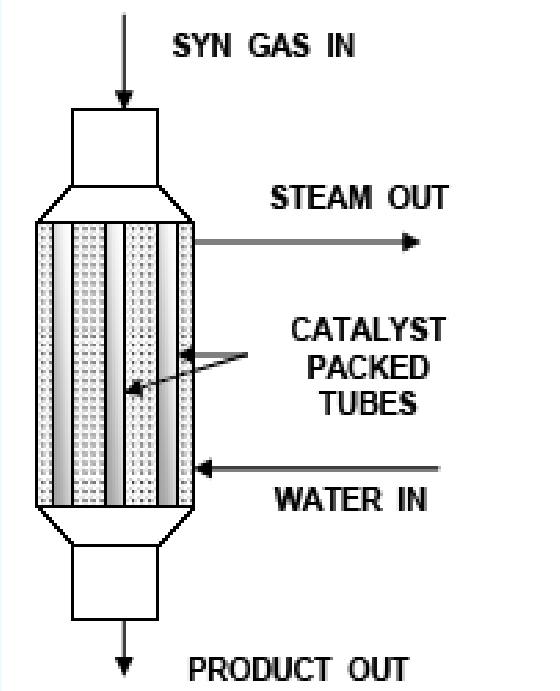
Available Technology: Fixed bed/Fluidized bed/Slurry bed

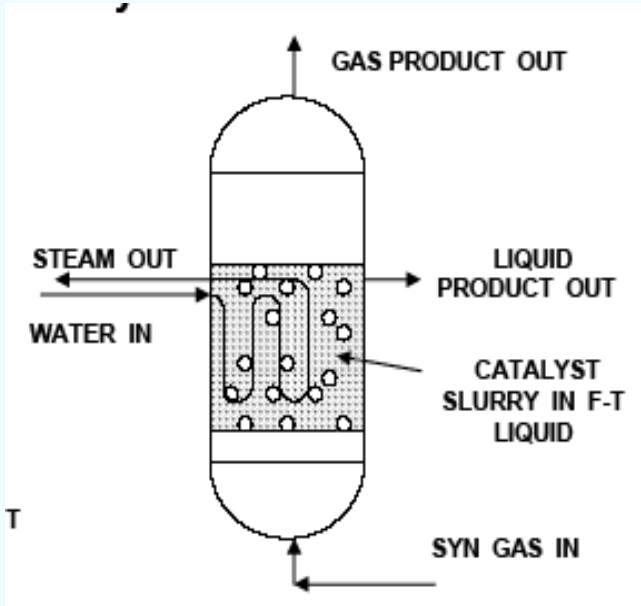
CO hydrogenation $nCO + 2nH_2 \xrightarrow[20\text{-}35\ bar]{180\text{-}350^oC} (-CH2-)_n + nH_2O$ -152 kJ/mol

Water gas shift $CO + H_2O \longleftrightarrow H_2 + CO_2$ - 41 kJ/mol

Methanation $CO + 3H_2 \longleftrightarrow H_2O + CH_4$ -206 kJ/mol

FT Reactor Types





Fixed Bed Reactor (FB)

- Multitubular design
- Diameter limited by slow heat removal
- Good for heavy liquid & waxes
- conversion per pass is limited, difficult to replace deactivated catalyst

Slurry Reactor

- Very high heat transfer rate
- High conversion per pass
- Higher catalyst activity with better selectivity
- Catalyst regeneration by continuous purge and feed
- Uniform temperature distribution
- Difficult to separate catalyst and Product

Product Refining

Long chain waxy HC (-CH2-)n → **Product Refining** → Naphtha, Kero, Diesel, Waxes

- Hydroprocessing Section
  - Hydroisomerisation / hydrocracking of n-paraffins to iso-paraffins of desired length & boiling range
  - Mild hydrocracking at 300-350 deg C & 30-50 bar
  - Reactivity increases with increasing number of paraffins
    - ✓ Maximum yield of middle distillates
    - ✓ Minimum yield of C4 & lighters
- Distillation Section
  - Conventional distillation for product fractionation
- Gas Processing & Wax Finishing as necessary

CTL Technology Development Efforts

EIL-BPCL-THERMAX-CHT

CTL Technology Development Approach

GASIFIER SECTION

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FT SECTION

CATALYST DEV
MICRO REACTOR
KINETIC DATA
COLD FLOW/CFD MODEL
REACTOR MODEL
DESIGN METHOD

DEMO PLANT

INTEGRATE A+B+C
FOR LARGE CAPACITY
PROCESS PACKAGE
ENGINNERING
PROCUMENT
COMMISIONING

Pilot plants and mathematical tools

- HPTGA
- Gasifier unit
- Syngas cleaning unit
- Cold stand Slurry column
- Facilities for catalyst formulations/testing
- Batch reactor/fixed bed/continuous for catalyst testing/FT kinetics

- Mathematical model
  - Gasifier
  - Slurry bubble FT reactor
  - CFD model of SBCR

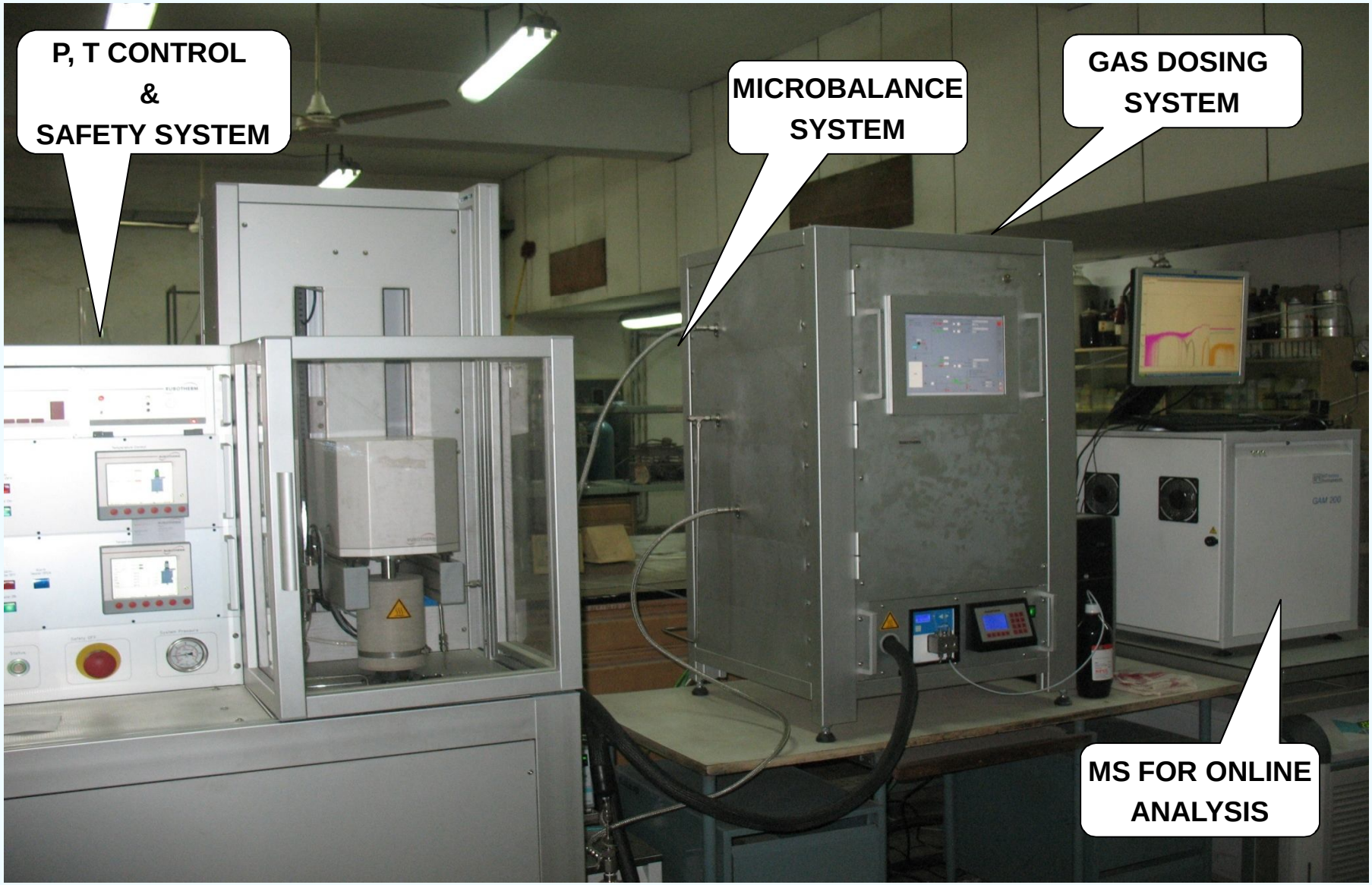
Gasification Studies: Kinetics Using HPTGA

- HPTGA along with MS for gas analysis have been installed at EIL-R&D complex
  - Design pressure: 50 bar
  - Design temp: 1100^0C
- Various type of coal viz. high ash coal, lignite, petcoke are being studied

Objectives:

- Investigations of coal gasification reactions at high pressure, high temperature, high ash coal
- Insights to Coal gasification 'reactivity'

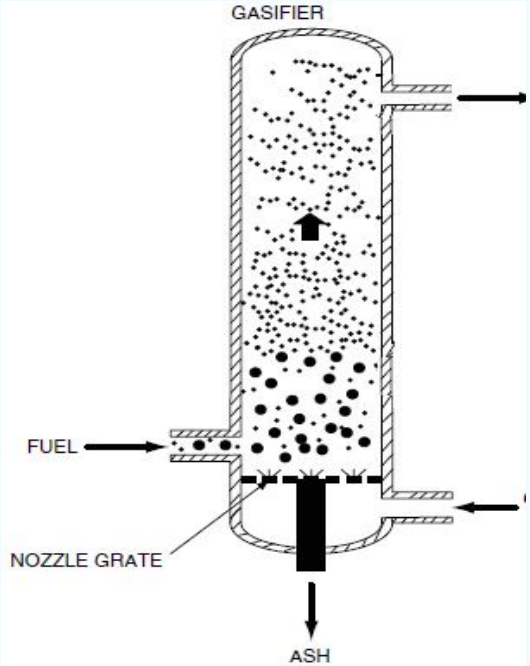
HPTGA + MS Expt. Setup at EIL, R&D Lab

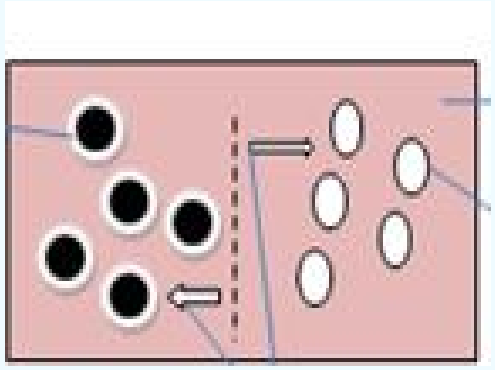


Mathematical Modeling of Gasifier

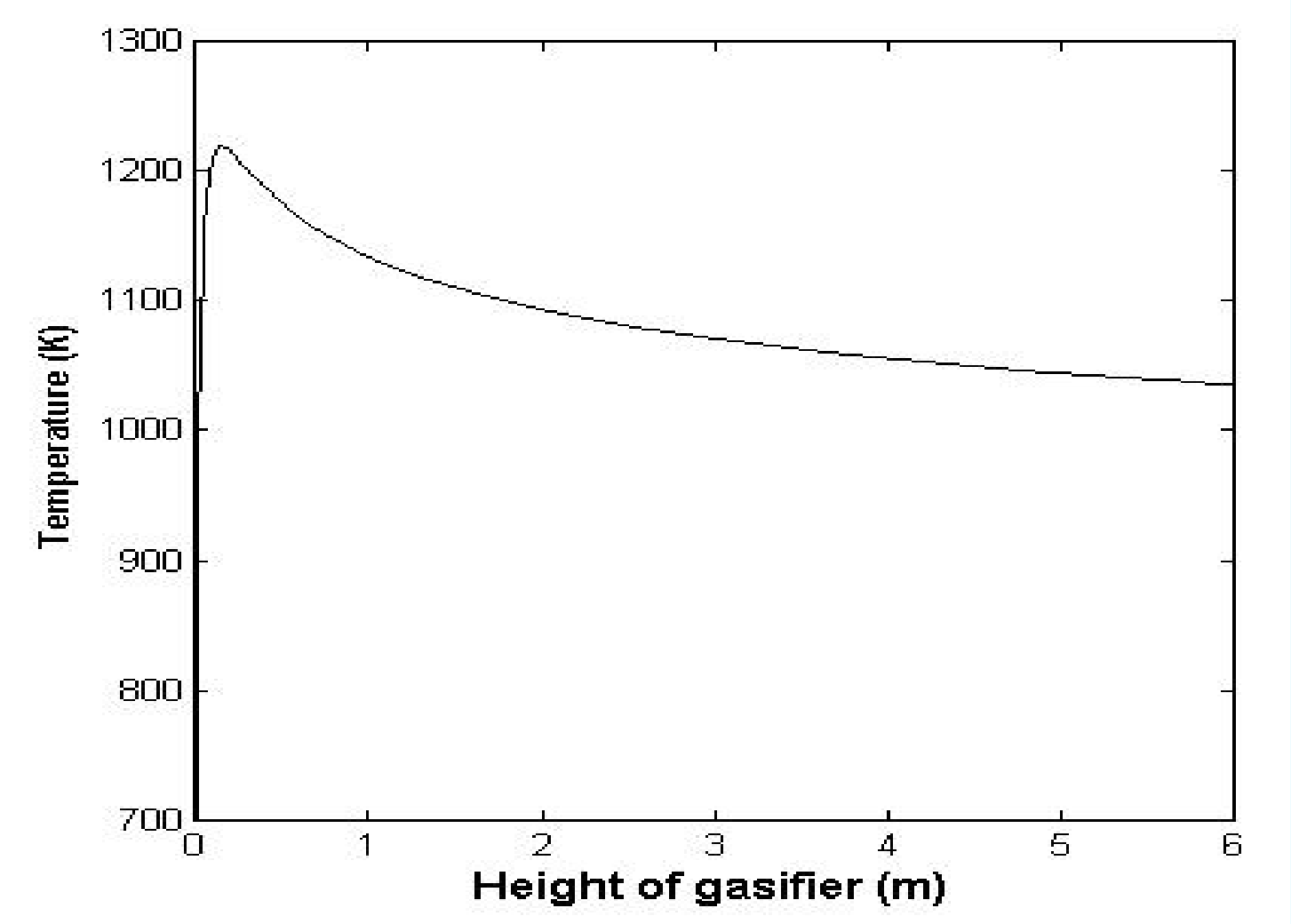
Issues of FBG at High Pressure

- Complex hydrodynamics
- Complex reaction kinetics (impact of ash layer not known)
- Kinetics at high pressure
- Multiphase, multi-component reactor modeling- solution is a challenge





Model Predictions



Gasifier Pilot Plant (FB Type)

- A coal gasification fluidized bed plant is designed and installed at EIL-R&D center
  - Capacity: 150 kg/h
  - O2 purity: 93% by volume

- The plant consists of
  - Coal crushing & feeding system
  - High pressure gasifier with ash removal system
  - Cyclones
  - Syngas cooling systems
  - Ash disposal system
  - Air separation unit, etc.

Gasifier And Syngas cleanup at EIL-R&D Gurgaon complex:

Pilot Gasifier: Issues being addressed

- **Process Design**
  - Coal Characterization and kinetics
  - Estimation of process parameters (T,P,C/O2, C/Steam, Flux etc)
  - Gasifier sizing (dia, height)
  - Quench System
  - Cyclone
  - Deep leg/j leg
- **Mechanical Design**
  - Coal preparation unit
  - Feed injection system
  - Ash/Solid removal
  - Loop seal
  - Distributor
  - Exchangers

Gasifier operation Strategy

- Operation was planned stepwise
  - Combustion
  - Gasification
    - Air mode
      - Gradual rise of pressure
    - Enriched O2
      - Gradual rise of pressure
    - O2& Steam
      - Gradual rise of pressure

Gasification experiments(Air mode)

SYN GAS FLARED IN GROUND FLARE WITH BLUE FLAME

Syngas Cleaning

- Gas Cleaning:
  - Removal of H_2S, COS, HCN, CO_2, NH_3, Particulates.
- Basis:
  - Adoption of Conventional Technologies & Novel Processes
- Pilot facilities created for syngas clean up
  - Water scrubber with EIL's proprietary structured packing
  - HCN/COS Converter
  - AGR unit

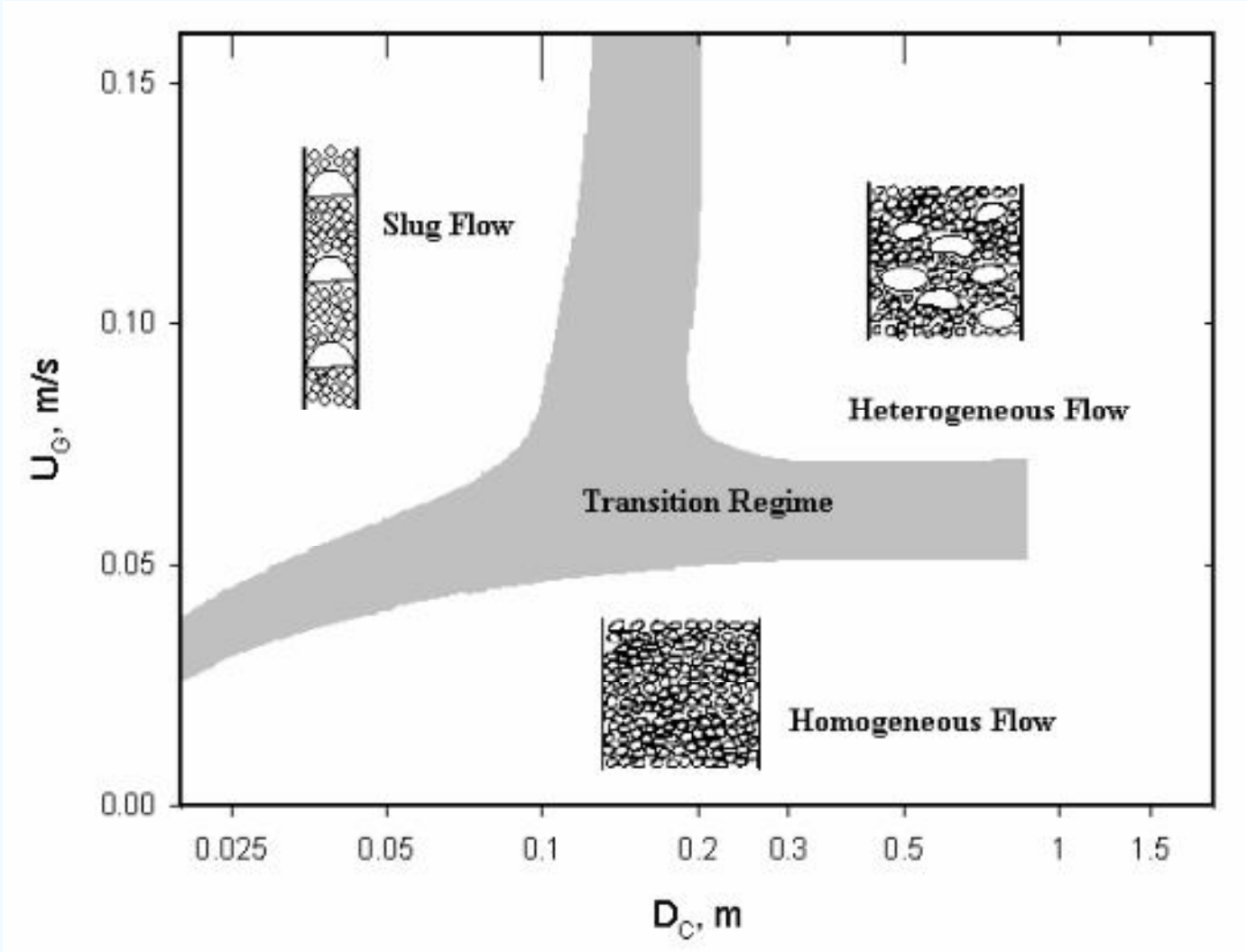
Syngas Cleaning Pilot Plant

Capacity: 350 Nm^3/h
Operating pressure: 30 bar

FT Technology Development Approach

- Catalysts & Kinetics (Iron/Cobalt based)
- Hydrodynamics of SBCR (Pilot plant/CFD studies)
- Development of mathematical model for SBCR
  - Conversion/Yield and selectivity/Sizing of reactors

Flow Regime/scale up issues



SBCR Pilot Plant at EIL, R&D

Effects of Various Parameters on Gas Holdup

Gas holdup & distribution of small and large bubbles affected by various parameters

- Superficial gas velocity
- Pressure
- Gas density
- Physical properties of liquid
- Solid concentration
- Reactor size
- Types of gas distributors

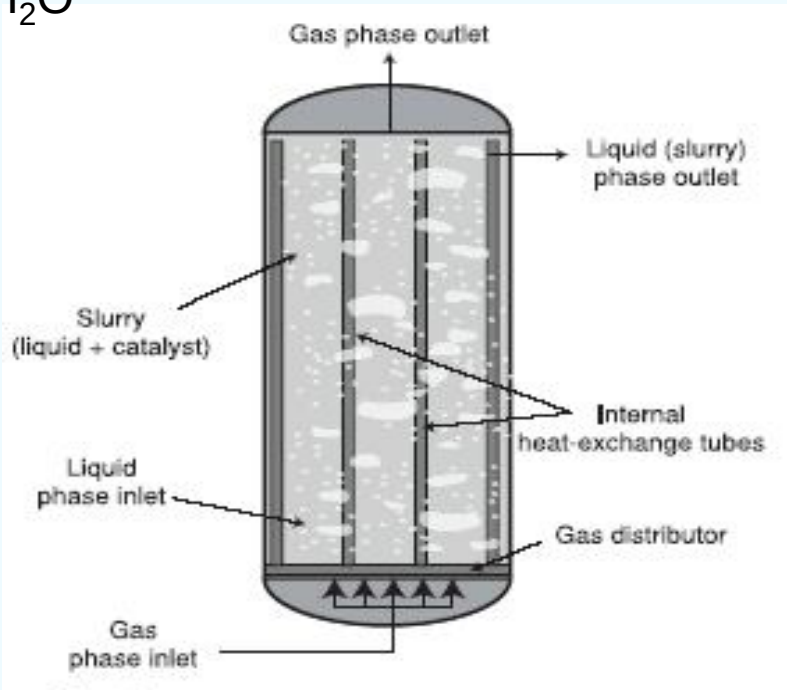
SBCR FT Reactor Modeling

- **Reactions:**

Paraffins: $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$

Olefins: $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$

Water gas shift : $H_2O + CO \leftrightarrow CO_2 + H_2$

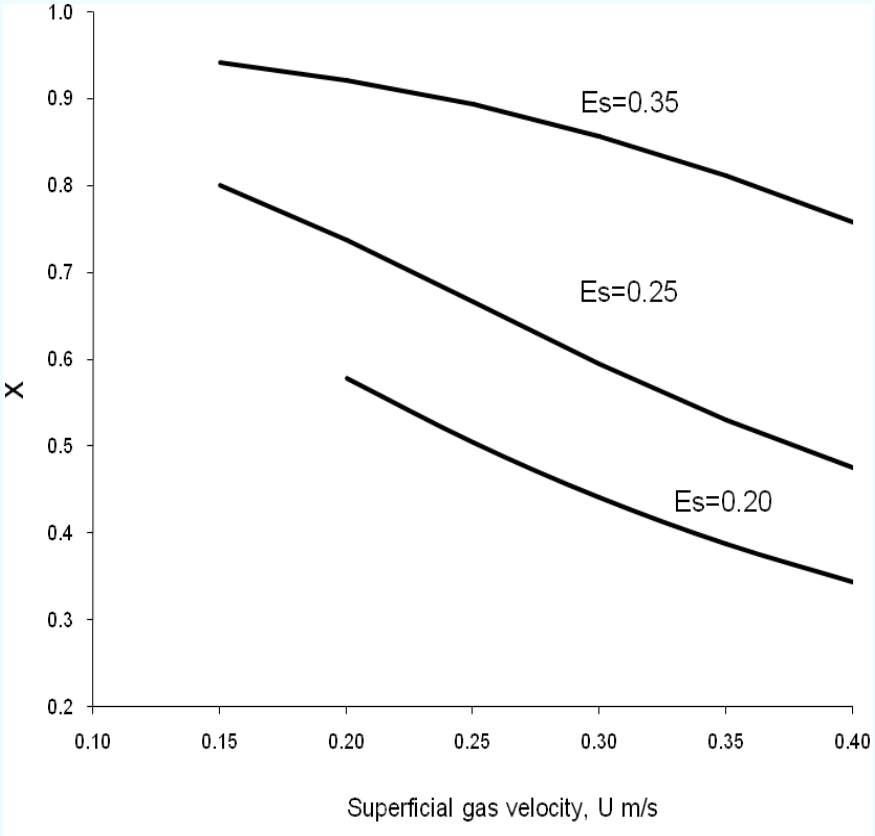


- **Kinetics (in-house with Co/Fe)**
- **Hydrodynamics (pilot plant, CFD)**

Target: The model can be used for

- **Design reactor**
- **Optimization & scale up**
- **Trouble shooting**
- **Control**

FT Reactor Model : Syngas Conversion



Comparison of Model Output		
	Lit	Model
Reactor details		
Reactor diameter (D_T), m	7	7
Dispersion height (H), m	30	30
Vertical cooling tube dia, mm	50	50
No of tubes	6000	5300
Operating conditions		
Temp, ^{0}C	240	240
Pressure (P), bar	30	30

BDEP of a Demonstration Unit

Broad aim

- Reasonably large size/integrating all the components.
- Locate near to a refinery site
- In long term demonstration of key components and carrying out wider range of experiments

BDEP/ capacity 1700 TPD high ash coal being prepared along with costing to demonstrate the technology and to understand the missing links if any

Summary

- CTL is an option for clean transport fuels will be attractive through technological advancement and reduced availability of oil and gas.
- Although CTL is known, still there several issues of design with high ash coal need to be assessed in Indian context.
- There are various technical components in CTL Process viz. coal gasification , syngas cleaning, FT synthesis and product upgradation.
- Experience of CTL with high ash coal is emerging. There are various issues to be experienced or to be assessed experimentally specially with gasification.
- EIL, BPCL, Thermax Ltd and CHT are engaged in developing CTL Technology based on high ash Indian coal.

Conclusions…

- Various sizes of experimental facilities have been created for gasification, syngas clean up, FT synthesis at EIL,R&D and BPCL,R&D to address various issues of design.
- Based on both experimental and Mathematical models it is planned to develop the complete CTL technology.
- Setting up a demonstration plant of capacity ~1700 TPD high ash coal is being assessed towards demonstration and commercialization of CTL unit
- It is hoped that numbers of offshoots technology will be useful and also will open several research front.
- Moreover syngas (an umbrella feed) will remain an answer to the chemicals, power, H2, SNG in crisis of gas/oil availability and will add flexibility in energy basket

Thank You

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DCL Vs ICL

	DCL Process	ICL Process
Coal to Liquefaction, TPD	4448	----
Coal to Gasifier, TPD	2136	9230
Total	6584	9230
Diesel, BPD	13090	13625
Naphtha, BPD	5389	6375
LPG, BPD	1521	--
Total products, BPD	20000	20000
Total Energy Input, BTU/D	186587	237432
Total Energy Output, BTU/D	112221	114857
Overall thermal Efficiency, %	60.14	48.37
Product yield, BBL of product per ton of dry	3.04	2.17
CO2 generation, kg/bbl of product	434	706

Syngas Cleaning & Conditioning

product	H_2/CO	total S	poisons	other
ammonia	∞	<100 ppbv	$CO + H_2O$ < 20 ppmv $O_2 + CO_2$ < 10 ppmv Cl < 100 ppbv P, As	$H_2/N_2 = 3.0$ inerts < 2%
hydrogen (by methanation)	∞	<100 ppbv	halides, As	$CO + CO_2$ < 2% O_2 < 1%
methanol	≈2.0 ($\underline{H_2+CO_2}$) ≈2.05 ($CO-CO_2$)	<100 ppbv	halides < 10 ppbv NH_3 < 10 ppmv HCN < 10 ppbv Fe/Ni carbonyls < 10 ppbv C_2H_2 < 5 ppmv unsaturates < 300 ppmv	CO_2 ≈ 3%
oxo alcohols	≈1.0	H_2S, COS, organosulfur	O_2, strong acids, HCN, dienes	CO_2 < 0.5%
MEG (for cryogenic H_2-CO separation)	1.5	<100 ppbv		CO_2 < 100 ppmv H_2O < 10 ppmv
SNG	3.0	<20–100 ppbv	halides, As	
Fischer–Tropsch (dependent on process)	1.3–2.6	<10 ppb to <1 ppmv	NH_3, HCN < 1 ppmv halides < 10 ppbv alkaline metals < 10 ppmv tars, phenols Hg, As, Se	
DRI	0.5–∞ ($\underline{CO + H_2}$) >2 ($CO_2 + H_2O$) preferred > 11	<0.3% preferred < 100 ppmv		N_2 < 6% preferred < 1% CH_4 3–4%

CTL Technology Components/Development Approach

Coal
C, H, N, S, O,
Metals (Fe,Ni,Na etc)
Ash

→

STEAM

↓

GASIFIER
$C + {}^1/_2\, O_2 = CO$
$C + O_2 = CO_2$
$C + 2H_2 = CH_4$
$CO + H_2O = H_2 + CO_2$

↑

Air/O2

→

SYN GAS
H_2
CO
CO_2
H_2O
CH_4

H_2S
COS
N_2
Ar
NH_3 + HCN
Ash/Slag/PM

→

Gas Cooling & Cleaning

↑ **Power MP/LP**

↓ CO_2, H_2O, H_2S, COS, NH_3 + HCN, Ash/Slag/PM

→

FISCHER-TROPSCH REACTOR
$CO+2H_2 \rightarrow -(CH_2)- + H_2O$
$CO+3H_2 \rightarrow CH_4 + H_2O$
$H_2 + CO = CO_2 + H_2$

→

PRODUCT UPGRAD/SEP PHYCAL SEP

↑ **FG C2/C3**

↓ **LPG NAPTHA DIESEL**

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INTEGRATE A+B+C
FOR LARGE CAPACITY
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→

COMPETITIVE TECHNOLOGY

LOOK BACK FOR UPGRADATION