Introduction to VR HCR

2011. 2. 23

GS Caltex Corporation

Company Overview

- The first private oil company in Korea as a JV between GS Holdings & Chevron in 1967
- Implemented energy business diversification and vertical integration

Refining & Marketing

CDU	840,000 BPSD
CNSU[1]	90,000 BPSD
RFCCU[2]	94,000 BPSD
Hydro Cracker	61,000 BPSD
KD-HDS[3]	262,000 BPSD
Market Share	29.8%
Service Station	3,574
LPG F/S	419

Petrochemicals

Aromatics
2,800 KMTA

Polypropylene
180 KMTA

Lubricants

Lube Base Oil
216000 BPSD

Lubricant
9,000 BPSD

Grease
8,000 Ton/Yr

Upstream

Cambodia
Block-A

Thailand L10/42
L11/43

Azerbaijan Inam
Block

Vietnam
Block-122

Subsidiaries & Affiliates

- GS Power
- Seorabeol City Gas
- Haeyang City Gas
- GS Nextation
- GS Fuelcell
- GS Nanotech
- AMCO
- GS Caltex S'pore
- GS Caltex (Langfang) Plastics
- GS Caltex (Qingdao) Petroleum
- GS Caltex (Qingdao) Energy
- Kangnam City Gas
- Kyungnam Energy
- Daehan Oil Pipeline
- Samnam PetroChem
- GS Park24

1. CNSU: Crude Naphtha Splitter Unit
2. RFCCU: Residual Fluid Catalytic Cracking Unit
3. KD-HDS: Kero Diesel Hydro Desulfurisation

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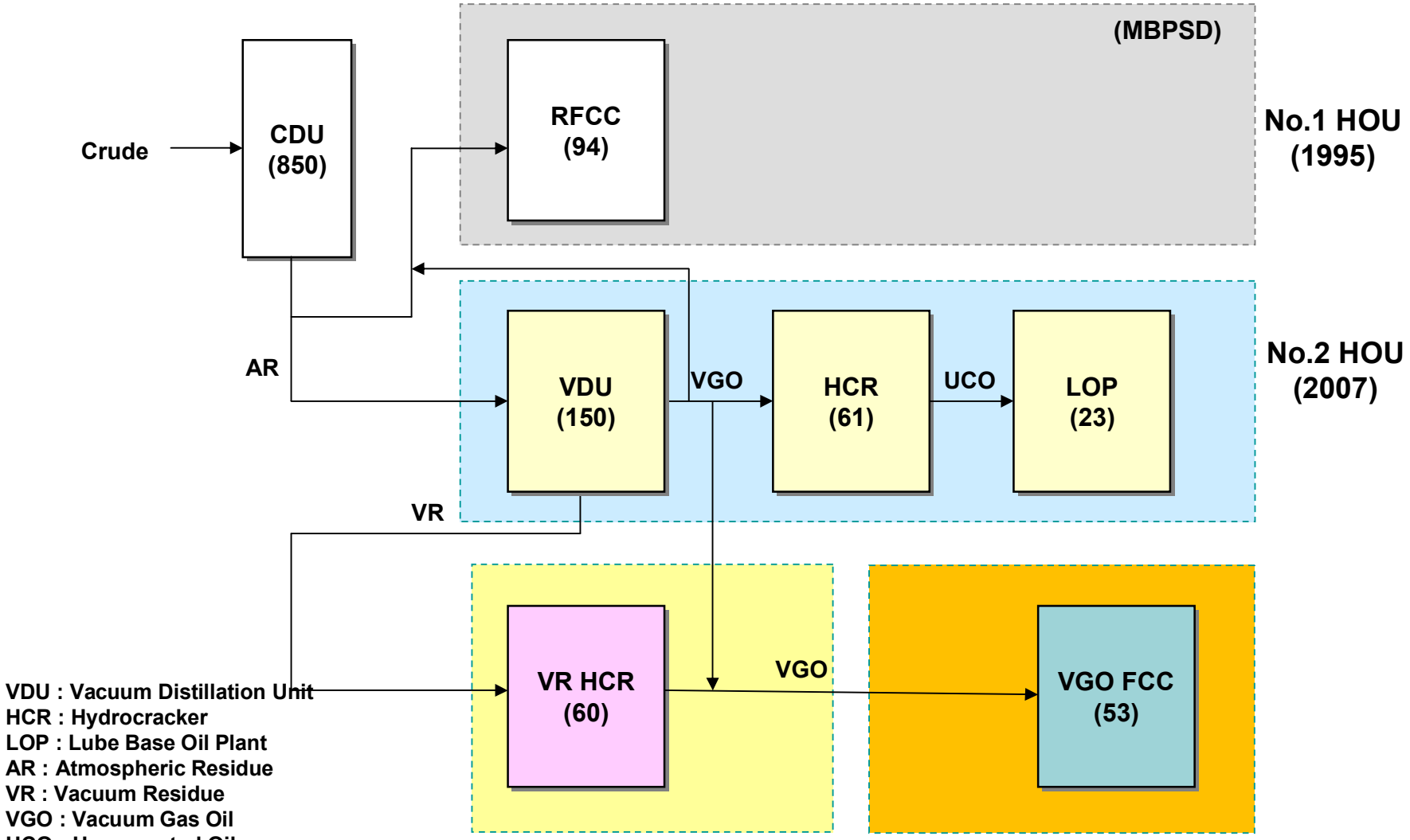
Integration of HOU Facilities

❑ GS Caltex Heavy Oil Upgrading Facilities



VDU : Vacuum Distillation Unit
HCR : Hydrocracker
LOP : Lube Base Oil Plant
AR : Atmospheric Residue
VR : Vacuum Residue
VGO : Vacuum Gas Oil
UCO : Unconverted Oil

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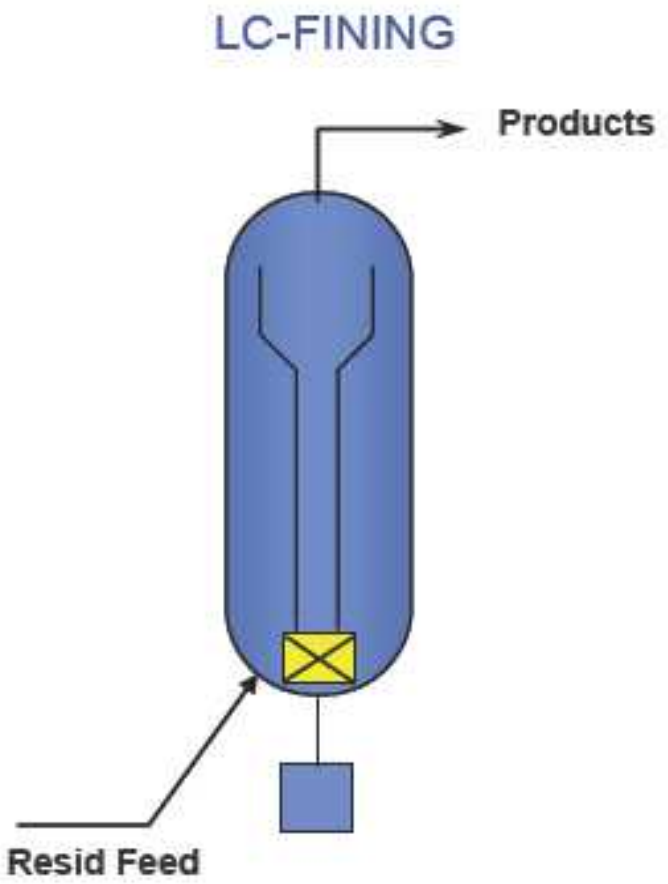
VR HCR ?

- **VR HCR: Vacuum Residue Hydrocracker**
  - Resid Feed(Vacuum Residue) with Hydrogen goes into Ebullated Bed Reactor at High Temp. & High Pressure (418^{o}C,180 Bar) .
  - VR Cracking & Removal of Sulfur, Nitrogen, and metal in VR
  - Kero / Diesel production
- **Available for Heavy and Sour (high metal/sulfur content) Feed**
  - AR (Atmospheric Residue)
  - VR (Vacuum Residue)
- **Ebullated Bed Reactor**
  - Isothermal Reactor Operation
  - No pressure drop build-up
  - Continuous Catalyst Make-up & Removal
  - Longer Run-length than Fixed Bed



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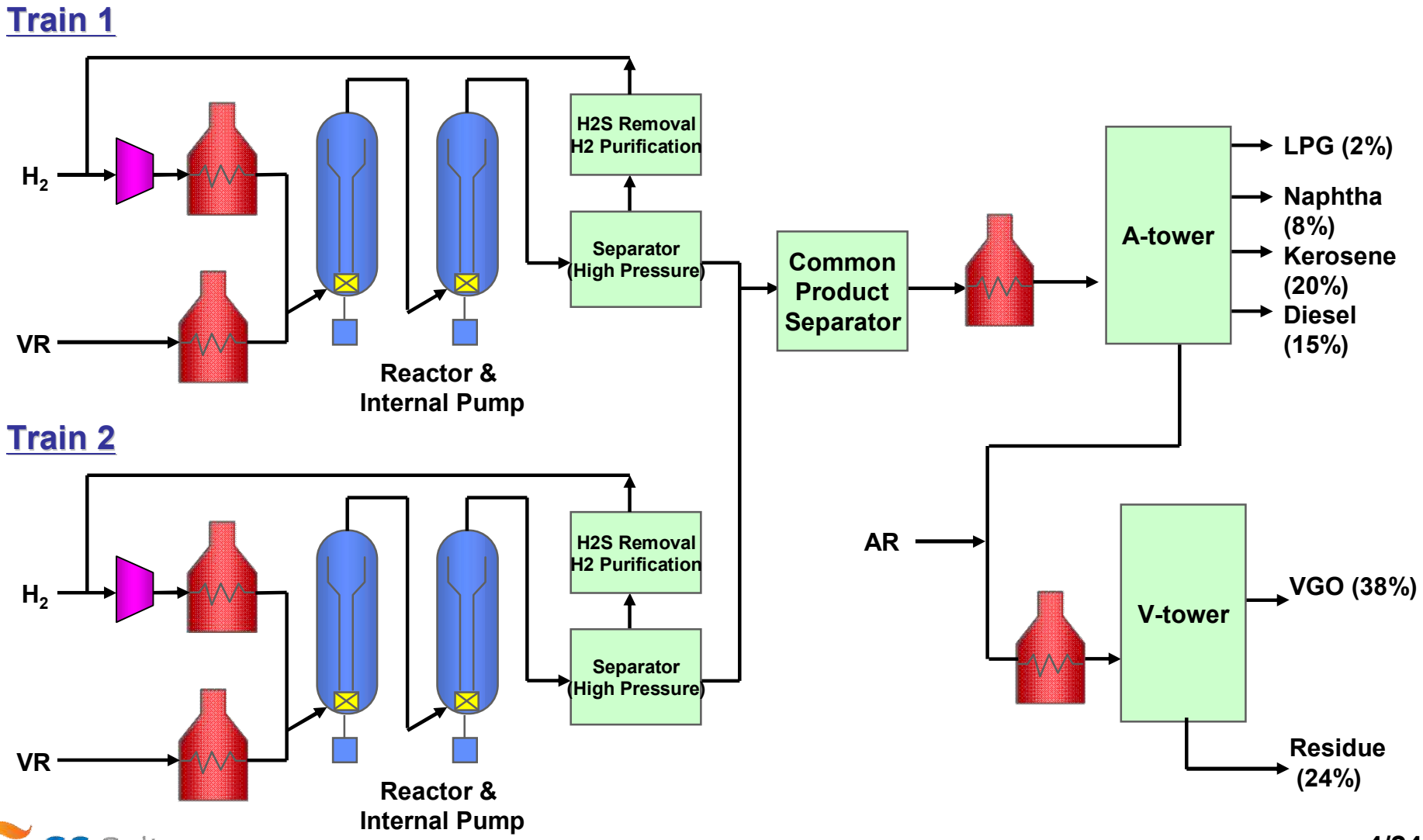
VR HCR Process Flow

2 Train Process at High Pressure, Common Separator, A-tower, V-tower



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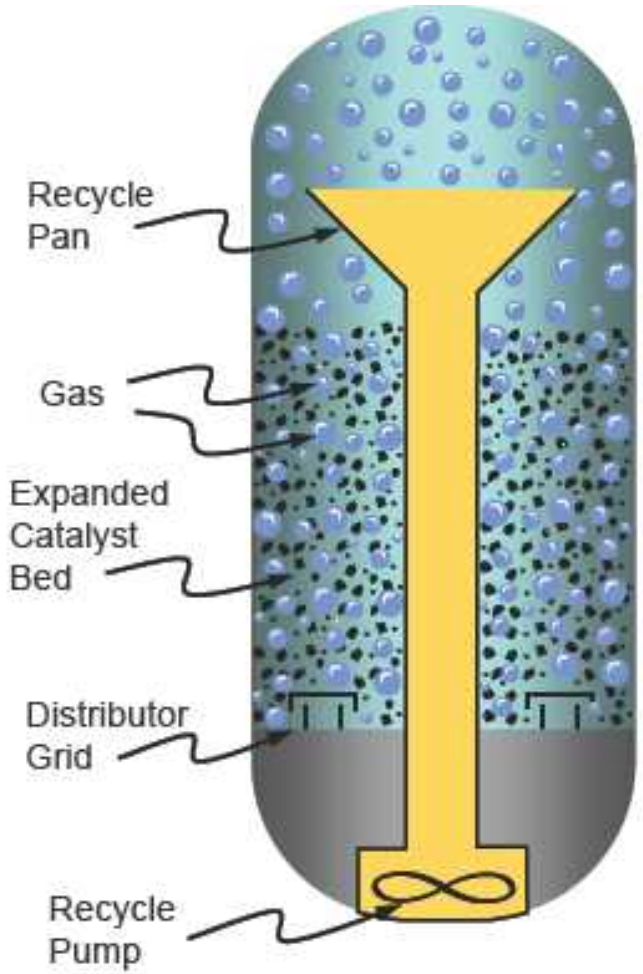
Ebullating Bed Reactor

- **Ebullating Bed Reactor**
  - Ebullating Catalyst with Using Recycle & Feed Flow
  - Control the Expandibility & Level of Catalyst Bed using Ebullating Pump.
  - Solid Handling

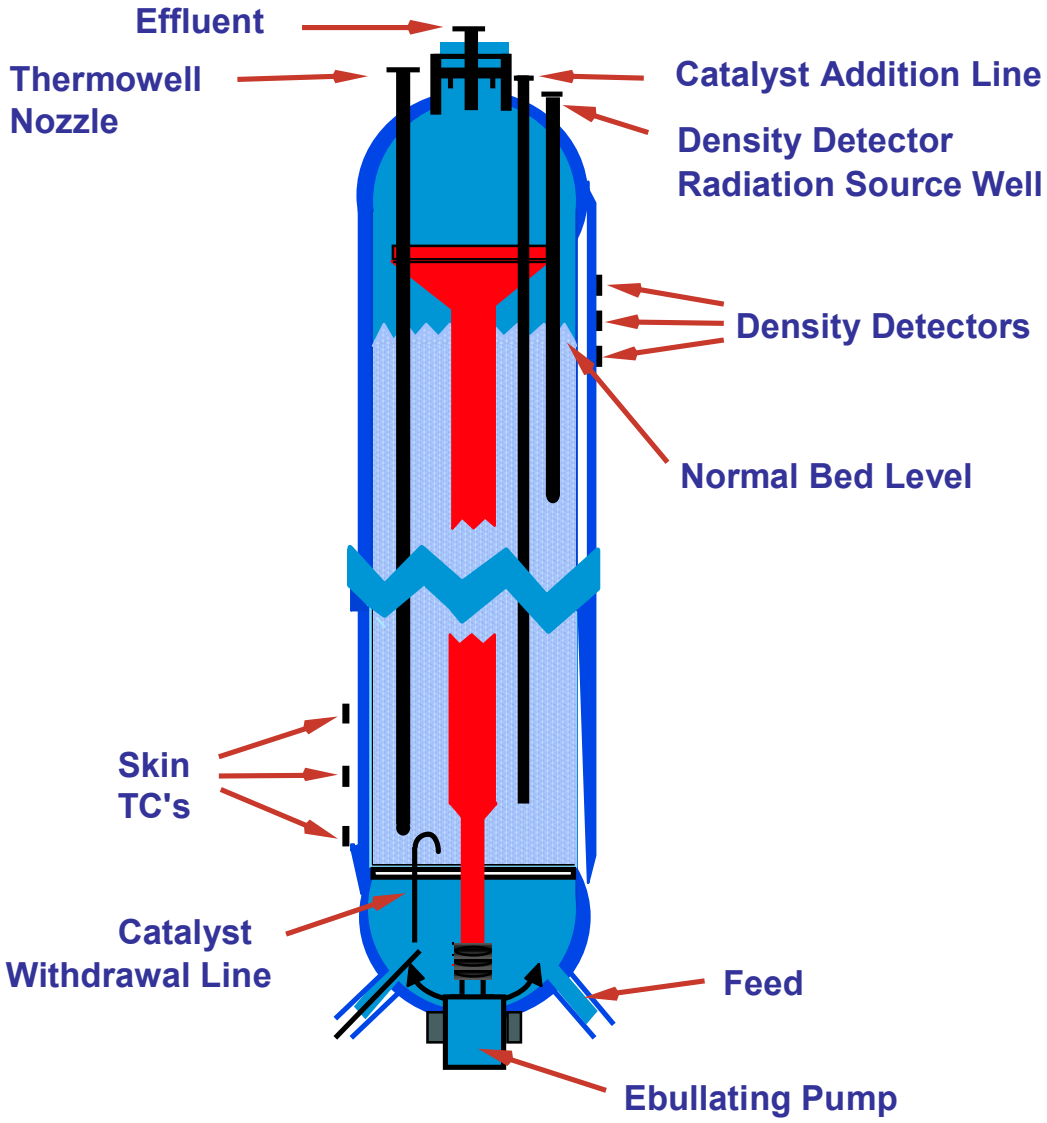
- **Advantages (vs. Fixed Bed)**
  - Isothermal
  - No pressure drop build-up
  - Continuous Catalyst Make-up & Removal
  - Longer Run-length than Fixed Bed

- **Operation**
  - Inlet Temp Control
  - Catalyst Level Control
  - Catalyst Make-up/Removal



Ebullating Bed Reactor

- **Reactor**
  - 4.1m x 49.5m
  - Operating Condition: 418'C, 170~180 KG (Base Case, 72% Conversion)
- **Ebullating Pump**
  - Flow Rate: 3000m3/hr
  - Pressure Drop: ~ 2KG
  - Modulating Catalyst Level with Recycle Flow Rate
  - RPM control with VFD
- **Recycle Pan**
  - Separating Gas / liquid
  - Liquid goes to EB pump through inner pipe
- **Cat. Handling Nozzle**
  - 4 Nozzle
  - Catalyst Making-up/Removal
- **Nuclear Detector**
  - Measuring Catalyst Level



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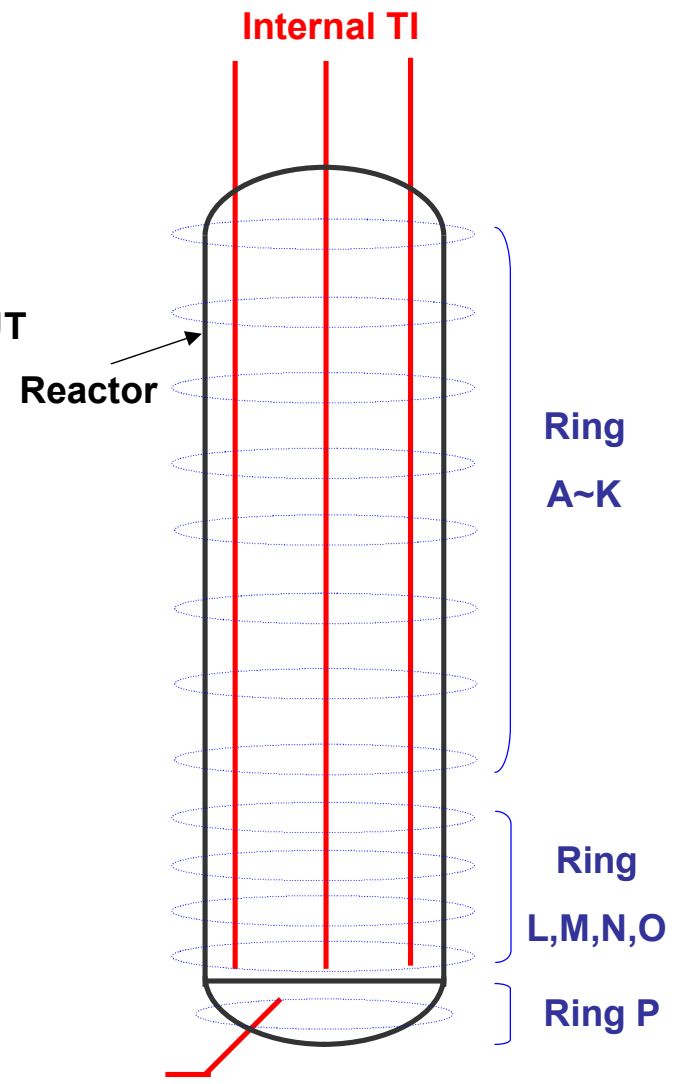
Temperature Surveillance

- ❑ Ebullating Bed Advantages (vs. Fixed Bed)
  - Isothermal
  - No Quench Gas needed
  - Less Catalyst Activity Decline

- ❑ Temp Surveillance ?
  - Temperature Monitoring Program for Reactor's IN&OUT
    - Measuring Avg. Reaction Temp.
    - Temp. Difference between IN&OUT
  - Purpose
    - Reaction Temp. Control
    - Cutback Initiator
    - Prediction of reactor's inner status
  - Total 132 TI Signal, (Scan Period=0.5sec)

- ❑ Process Upset
  - Hot Spot : Locally over reaction
  - Cold Spot : Coking Completed, No Reaction



Ebullating Bed Reactor

- Coke in Reactor (Upper Distributor Grid)

- Ebullating Pump

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Operating Condition

❑ Operating Variables

- Hydrogen partial pressure
- Temperature
- Catalyst Activity
- Space velocity (Feed Rate)

❑ Reaction Mechanism

- Cracking: Thermal Reaction
- Hydrogenation: Radical Capping, Hydrogenation, Product Stabilizing
- HDS / HDN / HDM / CCR Removal: Catalytic Reaction

Hydrogen Partial Pressure

- Increasing the hydrogen partial pressure increase the rate of reactions (first order in hydrogen partial pressure)
- Can be varied in a narrow range (by changing hydrogen purity) by either varying the recycle gas flow rate to PSA unit, or changing the hydrogen make up intake
- The pressure of the reactors in the train is controlled a 180-188 kg/cm2 (g) to maintain a hydrogen partial pressure of about 120 kg/cm2 (g) at the third reactor outlet.

Temperature

- Increasing the temperature increase the rate of reactions and the thermal cracking.
- Undesirable coking reaction and catalyst deactivation increase with increasing temperature.
- The temperature adjust the sediment level (HFT test) in reactor effluent. Fouling of the vacuum tower bottom rundown circuit has been experienced requiring frequent cleaning of the exchangers in this circuit.
- Fist reactor temperature controlled by hydrogen heater firing. Oil heater firing is base loaded. Second and third reactor temperatures controlled by injection of quench oil.

Catalyst Activity

- Increasing the catalyst activity increase the rate of reactions (more for HDS, HDN and HDM less for cracking).
- The catalyst activity level in the reactor is dependent on the addition rate of the fresh catalyst to and the withdrawal rate of the spent catalyst from the reactor.
- Catalyst addition rate set to achieve desired sediment or sulfur content of VR product (~4 t/d)

Space Velocity

- Increasing the space velocity increase the conversion
- Increased vapor rates reduce the liquid residence time and thus reduce the conversion.

Chemistry

- Cracking
  - Radical produced @ Thermal Cracking
  - Catalyst stabilize the radical with hydrogenation reaction.
  - Radical easily conversed to asphaltene/ coke Precussor
    - – Using Ebullating Bed, Maintaining high partial H2 Pressure, Control Catalyst Level. Slurry Oil Injection

- HDS, HDN, HDM

	Feed (wt%)	Removal (%)
HDS	4.68	80.0
HDN	0.32	34.7
Ni/V	30/97 wtppm	74.8/85.9

- Catalyst
  - HDS, HDN, HDM, and Hydrogenation
  - Coke and metal Laydown deactivate Catalyst

Fresh Catalyst	Content (wt%)
Aluminum Oxide	60-100
Molybdenum Trioxide	7-13
Aluminum Phosphate	3-7
Nickel Oxide	1-5

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Main Equipment

❑ High Pressure Reactor (4Ea)/ High Pressure Separator

❑ Membrane (2 Ea)

- Increasing Hydrogen Partial Pressure with Purifying Recycle Gas
- Remaining other gases(Nonpermeate) is for HMP(Hydrogen Manufacturing Plant)
- More Advantages for Membrane than PSA(Pressure Swing Absorber)

❑ Make-up & Recycle Compressor (5 Ea)

- Reciprocating Compressor
- Compensation Equipment for Membrane Pressure Drop

❑ Catalyst Handling System

- Fresh /Spent Catalyst Storage Equipment
- Diesel / HVGO Catalyst Transportation

❑ Chiller

- To reduce steam of the Vacuum Tower Ejector, Use Pre-Condensor/Chiller decrease Ejector Load.
- 3 Pre-Condenser, 5'C Cooling Water.

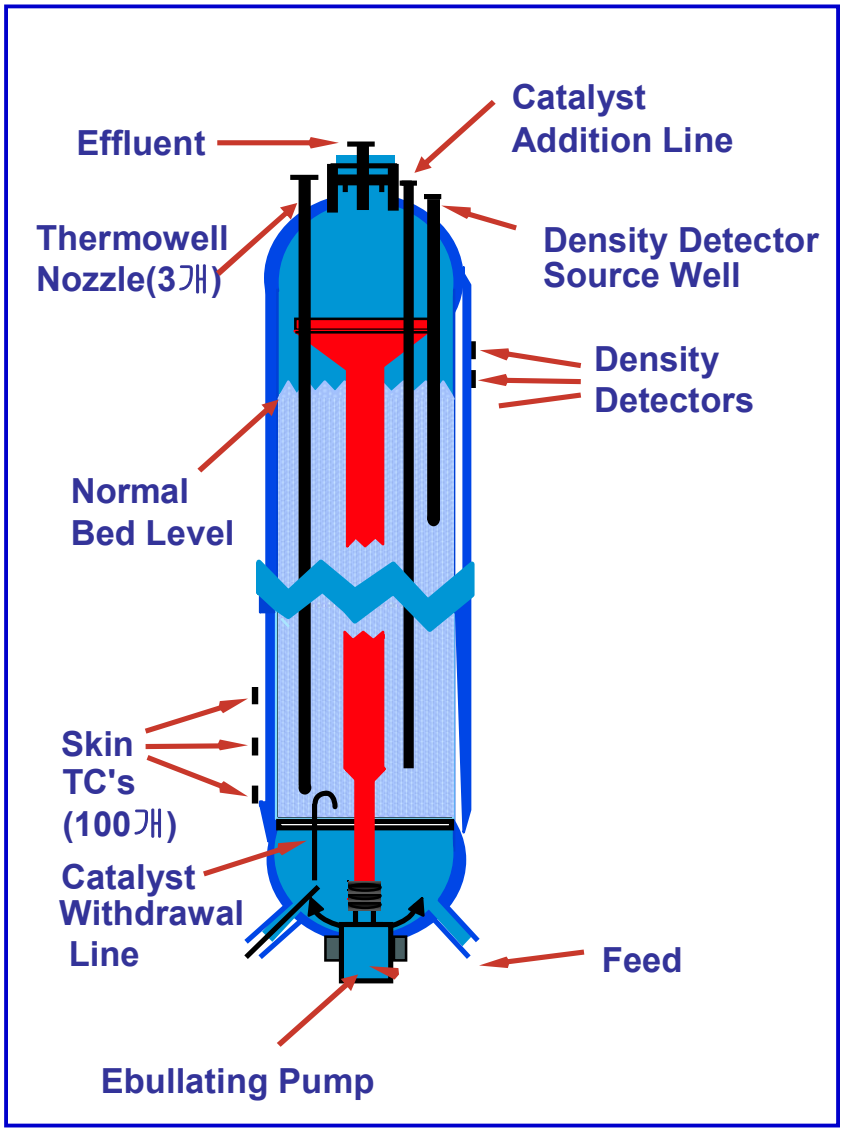
Details of VR HCR Process Operation (1/3)

❑ VR HCR Reactor

- Prevent Coking (Heat Accumulation) using Catalyst Ebullating Pump
- No Pressure Drop (ΔP < 2kg/cm2)
- Continuous Catalyst Make-up & Removal (Train: 3 times / 4days, 6 Ton/Day)
- Conversion: 72 % (from mainly thermal cracking reaction)
  HDS: ~ 80%

❑ Operation Considerations

- Coexist of VGO HCR & RFCC's problems
  Leak, Temperature Run Away (VGO HCR)
  Plugging, Coking (RFCC)
  -> Managing Operation Variables Rigidly
- Coking & Fouling Easily Happen
  -> Monitoring Operation Carefully
- In Emergency, Coking Formation !
  -> Needed Action Plan for Emergency
  (Minimizing Cut Back in Operation)



Details of VR HCR Process Operation (2/3)

❑ Conversion Constraints

- When Coking Formation Increases, Conversion should be Lowered Down.

Constraints	Effects	Actions
Feed Quality	Quantity of Coke Variation with Feed Quality	Monitoring/Analysis Carefully
Catalyst Activity	Activity Down, Sediment/Coke Formation Up	Normal Operation
H2 Partial Pressure	Hydrogenation Down, Coke Formation Up	Normal Operation

❑ The Relation between Feed Quality and Conversion

- Colloid Instability Index(CII): The Index of Determining VR HCR's Feed Quality, So called SARA
- When SARA (CII) Value is Small, High Conversion Reaction is Possible.

$$CII = \frac{Saturate + Asphaltene}{Resin + Aromatics}$$

→ Good Feed : Arabian, Kuwaiti, Iranian, Canadian heavy(vs Ural, Maya)

- Asphaltene Contents Up, Sediment Control Difficult
- High Molecular Wt. Asphaltene, Low Conversion Rate
- VR HCR Conversion = (Reacted 579℃+ Feed) / (Total VR HCR Feed)

Details of VR HCR Process Operation (3/3)

❑ Emergency Action

VR HCR Emergency Action: Prevent Coking Formation in VR HCR Reactor
-> Maintaining Catalyst Ebullation and Automatic Lowering Reactor's Temperature & Pressure

- **Cut Back**
  - **All Emergency Accidents of VR HCR are coped with Cut Back Program(DCS(Distributed Control System) Logic) without Operator's Manual Action.**
  - **But VR HCR starts the EDPS(Emergency Depressurizing System) program in Big Fire or Severe Leakage, Even though VGO HCR manually starts the EDPS.**
  - **The Initial Action for Emergency is important for preventing Coking Formation.**
  - **Frequent Cut Back is bad for Run Length & Conversion.**
  - **Cut Back is the Minimum Process Satefy Protocol.**
- **Kinds of Emergency**
  - **Fails to Ebullation**
  - **Abnormal Reaction Temperature**
  - **H2 or Feed Failure**

Cutback

- Cutback?
  - Automatic Program, Back to Stable Condition in Abnormal Reaction.
  - Coking easily happen in VR HCR at High Temp. Operation.
  - Cutback automatically starts when reactor's temp. radically up or Loss of Ebullation (catalyst level down).
  - Cutback decreases the reactor's temperature and pressure.
  - Mutiple Trouble for Multiple Cutback.

- Cutback Action
  - Action: Rx Temp High or Loss of Ebullation

CB Action, Reactor Temp High High	
Oil Heater	-25'C
H2 Heater	-50'C
Quench Oil Flow	+30 Sm3/hr
H2 Flow	To 75% of Normal SP
System Pressure	To 65% of Normal SP
Amine ABS	Bypass
Membrane	Trip

Catalyst Handling

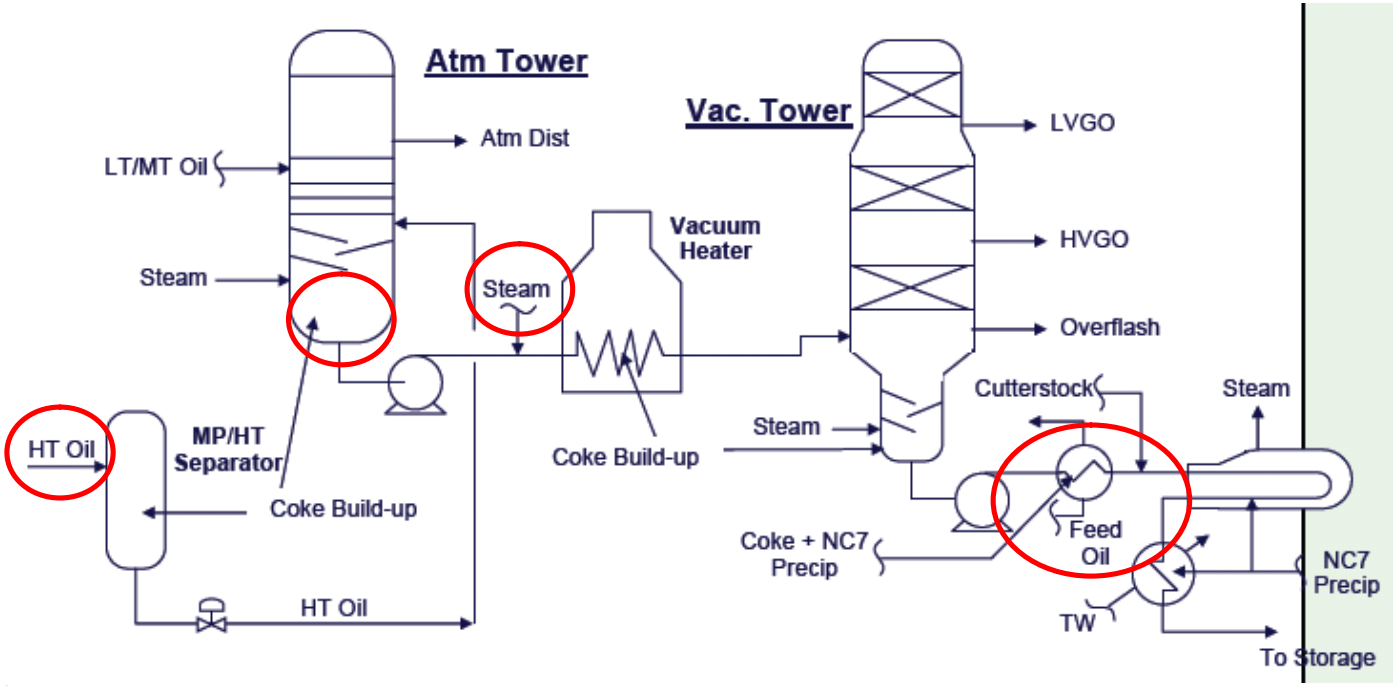
- ❑ To Maintain Catalyst Activity
- ❑ Continuous Fresh Catalyst Injection & Deactivated Catalyst Removal

- ❑ Operation
  - Catalyst Handling Section
  - Sequence Program: Automatic Program for Continuous Catalyst Injection & Removal
  - Batch Operation
  - Fuctions
    - Fresh Catalyst injection and storage
    - Initial Catalyst Charging

Maintenance Issues 1

- 64% of Shot Down is from Equipment Trouble.
  - Fouling: Damage of Heat Exchanger & Pipe
  - Solid Handling: Valve Damaging

- New Application
  - Separation of Oil/H2 Heater
  - Velocity STM to V-Tower Heater
  - VTB Circuit Heat Exchanger: 50% Spare, Cleaning 1 time per 2~6 week
  - Special Ball Valve : Pipe for Catalyst Transportation



Maintenance Issues 2

- VTB R/D Circuit H/ex

- Column Internal

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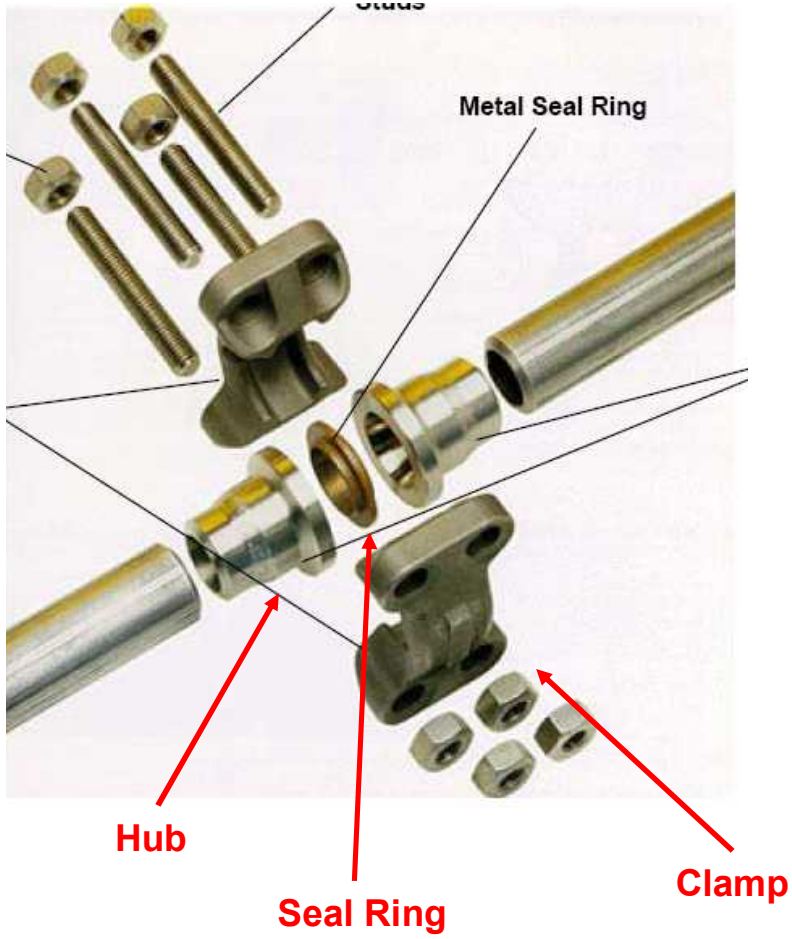
Clamp Connector

- ❑ Clamp Connector?
  - Good Sealing Performance
  - Self-Energizing

- ❑ Consist
  - Hub : End Flange
  - Seal Ring : Between Hub
  - Clamp

- ❑ Application
  - High Pressure Pipe (over #4500), Critical Service
  - Pipe for Reactors



Summary

- Ebullating Bed Reactor
  - Ebullating Catalyst with Using Recycle & Feed Flow
  - Isothermal, No pressure drop build-up
  - Continuous Catalyst Make-up & Removal
- Operating Variables
  - Hydrogen partial pressure
  - Temperature
  - Catalyst Activity
  - Space velocity (Feed Rate)
- Cutback
  - Automatic Program, Back to Stable Condition in Abnormal Reaction

Thank you very much

Email: jhseok@gscaltex.co.kr

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