Catalytic Reforming for Aromatics Production

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Role of Catalytic Reforming

- **MAIN PROCESS FOR UPGRADING LOW OCTANE NAPHTHAS TO HIGH OCTANE GASOLINE BLENDING COMPONENTS OR CHEMICALS INTERMEDIATES (BENZENE/TOLUENE/XYLENES)**

- **NUMBER OF IMPORTANT BYPRODUCTS**
  - H$_2$ FOR HYDROTREATING
  - C$_1$-C$_2$ FOR FUEL GAS
  - C$_3$-C$_4$ FOR LPG
  - C$_4^+$ TO MOGAS OR ALKYLATION (IC$_4^+$)
  - AROMATICS FOR CHEMICALS

- **MODERN CATALYTIC REFORMING DEVELOPED IN THE EARLY 1950'S WITH DEMAND FOR INCREASED GASOLINE OCTANE**

- **SIGNIFICANT IMPROVEMENTS OVER THERMAL REFORMING**
  - HIGHER OCTANE AND YIELD
  - BETTER QUALITY (SULPHUR, DIOLEFINS)
Process Description

- Naphtha feedstock
  - Typical C 6 to C 10
    - Feed tailored to the desired product C 6 to C 8 is better
    - Fractionated to remove heavy ends
  - Hydrotreated to remove
    - Sulfur
    - Nitrogen
    - Olefins
    - Oxygenates
    - Metals
  - Paraffins, naphthenes and aromatics
  - Combined with hydrogen rich recycle gas
  - Vaporized in feed effluent heat exchangers
    - Necessary to be all vapor before heater
Process Description Continued

• Feed and recycle gas
  • Heated to reaction temperature in furnace
  • Introduced to first reactor
    • Desired reactions are endothermic
    • Strong endotherm in first reactor reaching a reaction quench temperature
  • Followed by 2 to 4 additional reactor heater combinations
    • Entire reaction train in vapor phase
Simplified Semi-Regen Reformer
Cyclic Reforming

HYDROFINED NAPHTHA FEED

A - S

REACTORS

UPPER REACTION HEADER
UPPER REGEN HEADER

FIRST REHEAT FURNACE
SECOND REHEAT FURNACE
THIRD REHEAT FURNACE

LOWER REACTION HEADER
LOWER REGEN HEADER

PREHEAT FURNACE

TO/FROM REGEN CIRCUIT

TO EFFLUENT EXCHANGERS, SEPARATOR DRUM, ETC.
UOP CCR Reformer

Regenerator

Regenerated Catalyst

Spent Catalyst

Cat Flow

Hydrogen

Hydrotreated Naphtha Charge

Start

#1

#2

#3

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Unit Revamps

• Most done to stretch existing unit capacity
  • Heater preplacement due to creep
• Lowering pressure to increase yields
  • Changing feed effluent exchangers
  • Purge from compressor discharge
• Switching from mono metallic catalyst to bi metallic catalyst
Catalyst

• Dual Function
  • Acid: Alumina with chloride
  • Metal: Pt with or without promoter metals (Re, Ir, Sn)
    • Re provides coke stability and additional run length  Sulfiding required
    • Ir additional activity  Sulfiding required
    • Sn promotes yield at low coke levels  no sulfiding required

• Supported on gamma alumina
  • High surface area
    • 200 m²/gm fresh catalyst
    • 120 m²/gm aged catalyst
      • Surface area decline with exposure to high temperature and steam

• Heart of reforming process
  • Promotes “good reactions”
Products

• **SAME HYDROCARBON TYPES AS FEED BUT PRIMARILY AROMATIC AND C7- PARAFFINS**

• **AROMATICS ARE THE PRINCIPAL SOURCE OF HIGH OCTANE**
  • NAPHTHENES AND C8+ PARAFFINS ESSENTIALLY ABSENT AT 98+ RON
  • LIGHTER PARAFFINS ARE MORE BRANCHED THAN IN FEED BUT ARE STILL PREDOMINATELY SINGLE METHYL SUBSTITUTED WITH LOW RON
Unit Optimization

• Low pressure and low H2 / HC ratio favor
  • Higher liquid yields
    • Higher aromatic yields
  • Coke

• High temperatures favor
  • Dehydrogenation
  • Dehydrocyclization
  • Hydrocracking
  • Coke
Feed Selection

• High yield- Easy feed
  • Naphthenic feeds
    • Example Sleipner Condensate
      • ~70% naphthenes
    • Require large reheat furnaces- high endotherms
    • High hydrogen and aromatics yields

• Lower Yield – More difficult feed
  • Paraffinic feeds
    • Example Lt Arab Naphtha
      • ~ 70% paraffins
    • Reactor endotherms decreased
    • Higher Lt ends yields
Mogas Vs Aromatics Operation

• Mogas operation
  • Targets C5+ RON needed for gasoline blending
  • Target can and will change based on gasoline grade blended
  • Typical RON 92 to 95 with short excursions to 98 as needed

• Aromatics operation
  • Target maximum aromatics concentration in reformate
  • Typical RON of reformate > 98 with some units operating up to 102
    • Feed and unit type dependent
    • Semi regen units require frequent regeneration
    • Cyclic and CCR better suited for aromatics operation
  • Minimize C9 non aromatics
Yield versus Severity

Typical yield with a feed Watson K of 11.8
Expected Yields

Reformer Types and Yields

- Cyclic
- Semi Regen
- Semi Regen 2
- CCR

Yield

Months

Reflection Types and Yields
Aromatics Recovery

• Remove light ends
  • Depentanize via distillation

• Remove heavy ends
  • C8- overhead in distillation tower
    • Can separate A8 from A9 by distillation
    • Cannot separate A8 from P9 by distillation
      • Azeotrope formed
  • Mogas and / or aromatic solvents

• C6 to C8 stream sent to solvent extraction
  • Raffinate to mogas or specialty solvents
BTX Recovery

• Clay Treater

• Fractionation
  • BZ product O/H
  • Tower bottoms to another fractionator
  • Toluene product overhead
  • Tower bottoms to another fractionator
  • Tower overhead concentrated Para Xylene
    • Sent to Parex for production of pure Px
    • Parex reject stream sent to Para Xylene Isomerazation
  • Tower bottoms sent to another fractionator
    • Produces Ortho Xylene from tower overhead
    • Tower bottoms sent to mogas
Additional Px

- Product Toluene is divided between sales and STDP
  - Flow rates determined by economics
  - STDP Feeds Toluene
    - Major product are
      - Benzene
      - Para xylene