History, Stories, and Lessons Learned from Resid Hydrocracking Development

Joe McLean
Astron International / RefComm
Ebullated Bed Reactor

- Invented by Edwin Johanson – Hydrocarbon Research Inc. (HRI)
  - Patent filed 1961 – granted 1965
Let’s Clarify Some Terminology

• Ebullated or Ebullating?
  • Ebullated refers to the state of the reactor catalyst bed
  • Ebullating refers to the pump that creates the condition
  • (think fluidized vs. fluidizing)

• Is it really Resid Hydrocracking?
  • Catalytic Hydrocracking (VGO feed) uses dual function catalyst / reaction scheme
    • Acidic cracking function – amorphous or zeolite (carbenium ion mechanism)
    • Active metals for hydrogenation
  • These heavy resid systems are too deactivating for acidic cracking catalysts
    • Conversion is thermal at reaction conditions employed (free radical mechanism)
    • Catalyst plays multiple roles
      • HDS / HDN / (HDO) / capping cracked fragments with hydrogen
      • Partial ring saturation for higher reactivity
    • Key is to balance thermal and catalytic reactions
Ebullated Bed Process Features

- High ratio of internal recycle to fresh feed
  - Near isothermal operation
  - Provides velocity to keep catalyst bed fluidized in three phase system
- Continuous catalyst addition and withdrawal
  - Not restricted by cycle lengths and changeouts
  - Constant operating conditions and product quality
- Kinetically – functions as a back mixed reactor or CSTR
  - Limits conversion
  - Partially addressed by staging
Early Development History

- H-Oil – initially by HRI
- First demo unit (2.5 KBPD) at Cities Service (now Citgo) Lake Charles LA refinery
- First large commercial unit at KNPC (Kuwait) in 1968 – 30 KBPD
- Joined by Lummus for engineering and licensing
  - LC-Fining was Lummus and Cities
- HRI / Lummus parted ways and pursued parallel developments
  - Some design differences but largely equivalent
  - In retrospect – this was probably bad for both sides due to market size
- H-Oil unit explosion and fire at Esso Bayway in 1970 was a major obstacle
  - HRI believed a comprehensive analysis provided exoneration
Development History 1970’s-80’s

• High oil prices and supply uncertainty (two oil embargoes) provided incentives for upgrading

• Major focus on synfuels development involved both HRI (H-Coal) and Lummus

• Canadian oil sands development provided opportunities

• “Flagship” units started up
  • Texaco Convent (later Motiva / Shell) H-Oil 52K BPD 2 trains / 2 stages
  • Amoco Texas City (later BP / Marathon) LC-Fining 75K BPD 3 trains / 3 stages
Early Challenges

• Reliable operation of catalyst addition / withdrawal and maintenance of catalyst activity
  • Multiple catalyst suppliers involved in catalyst development – good base load for manufacturing!

• Heavy product stability
  • “Antisolvent precipitation” of asphaltenes led to product quality issues as well as operating problems in downstream separators
  • Use of aromatic solubility agent such as FCC HCO implemented (be careful about non-reactive refinery recycle loops!)
Process Improvements Identified

• Staging
  • Improved kinetic driver for conversion
  • Heat of reaction control with additional H2 addition
  • Possible interstage product separation
  • Backwards cascading of catalyst (mimic fixed bed catalyst grading)

• Vacuum bottoms recycle for max conversion (e.g. 95%+)
  • Demonstrated in pilot scale and designed for Convent but never (?) implemented
A few comments on H-Coal

- Process, modelling, and equipment developments could be “cross fertilized”
- Very severe service due to solids levels in slurries
- Chemistry differences – very aromatic products
- Joint government / industry program – DOE, EPRI, HRI, Mobil, Amoco, Arco, Ashland
- 250 TPD Coal (~800 BPD products) demo plant in Ashland’s Catlettsburg KY refinery operated 1979-1985
- Today – direct CTL would face severe GHG issues beyond economics
Some Later Events 1980’s Onward

• High Oil price predictions ($>100/B) never materialized
• Reagan Administration severely curtailed synfuels programs
• Tough times for HRI
  • ~70% downsizing
  • Sold to Husky Oil as part of H-Oil license agreement
• Husky later sold HRI to IFP – became part of Axens in 2001
• Lummus joined with Chevron to form CLG alliance