

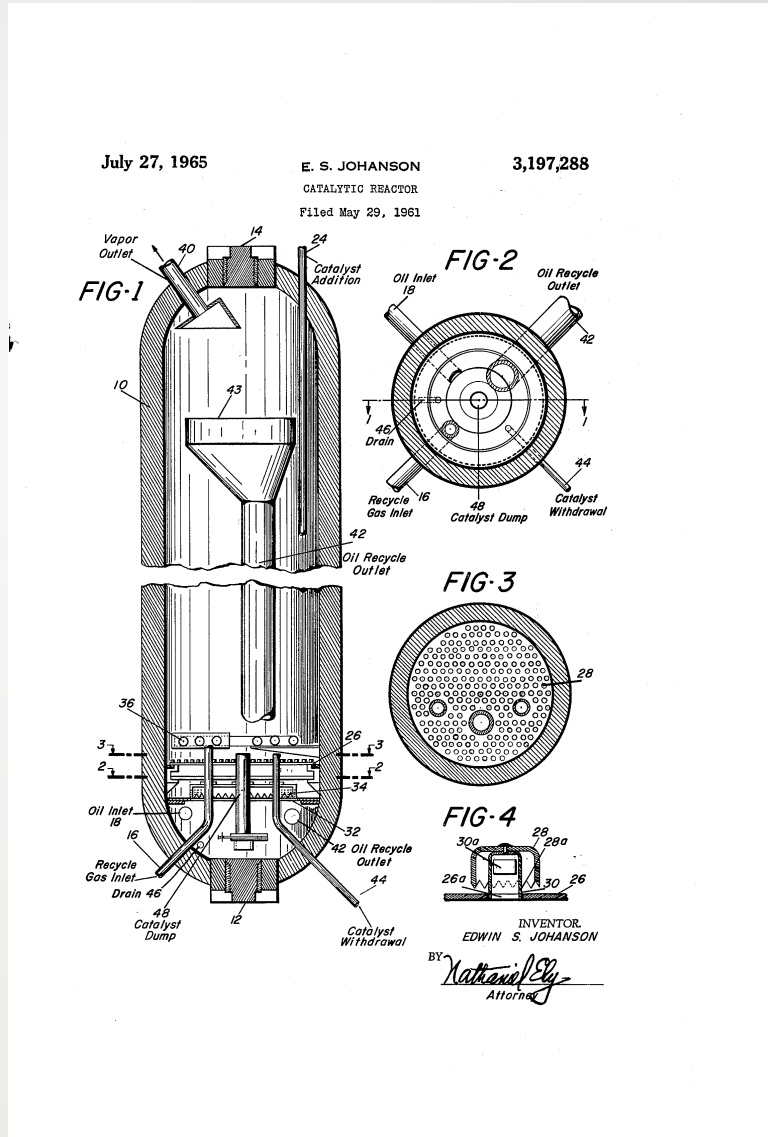
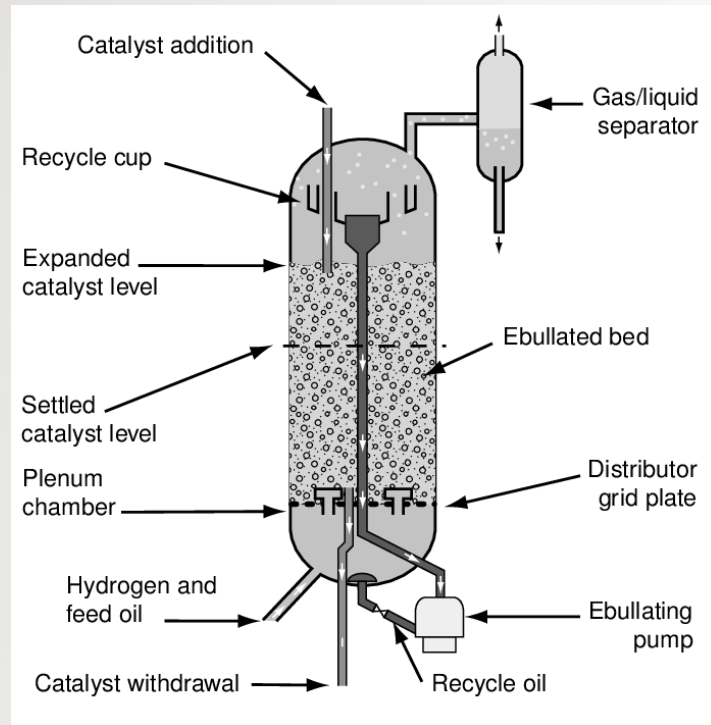


History, Stories, and Lessons Learned from Resid Hydrocracking Development

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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

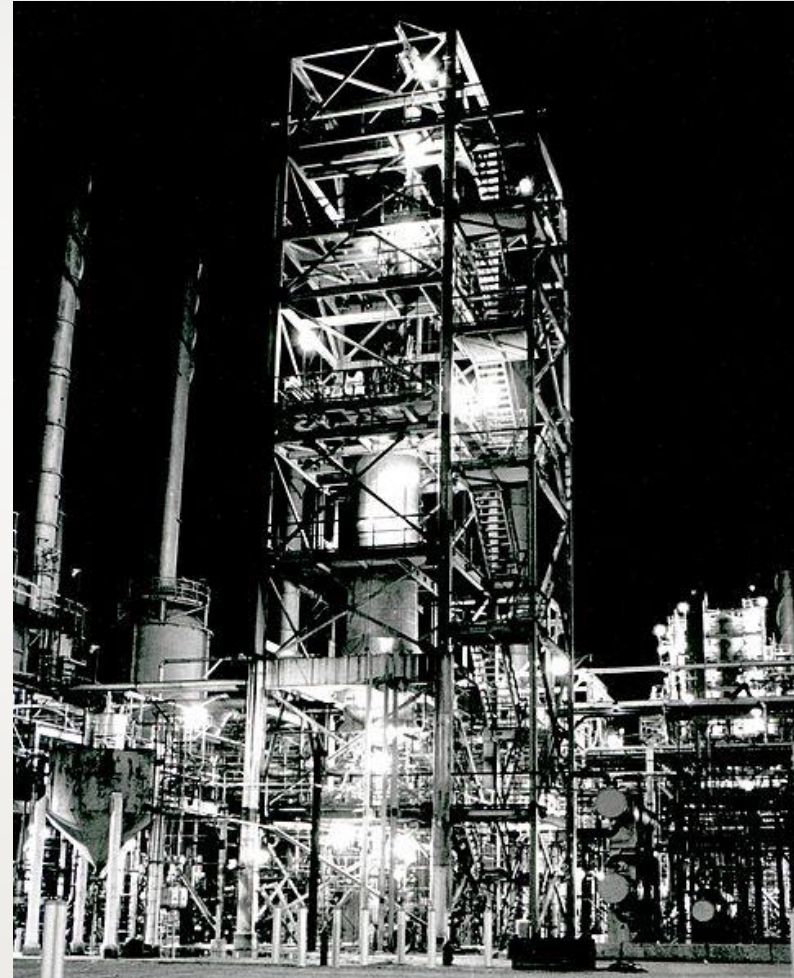
- Reliable operation of catalyst addition / withdrawal and maintenance of catalyst activity
 - Multiple catalyst suppliers involved in catalyst development – good base load for manufacturing!
- Heavy product stability
 - “Antisolvent precipitation” of asphaltenes led to product quality issues as well 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