100 Years of Scaling Up Fluidized Beds

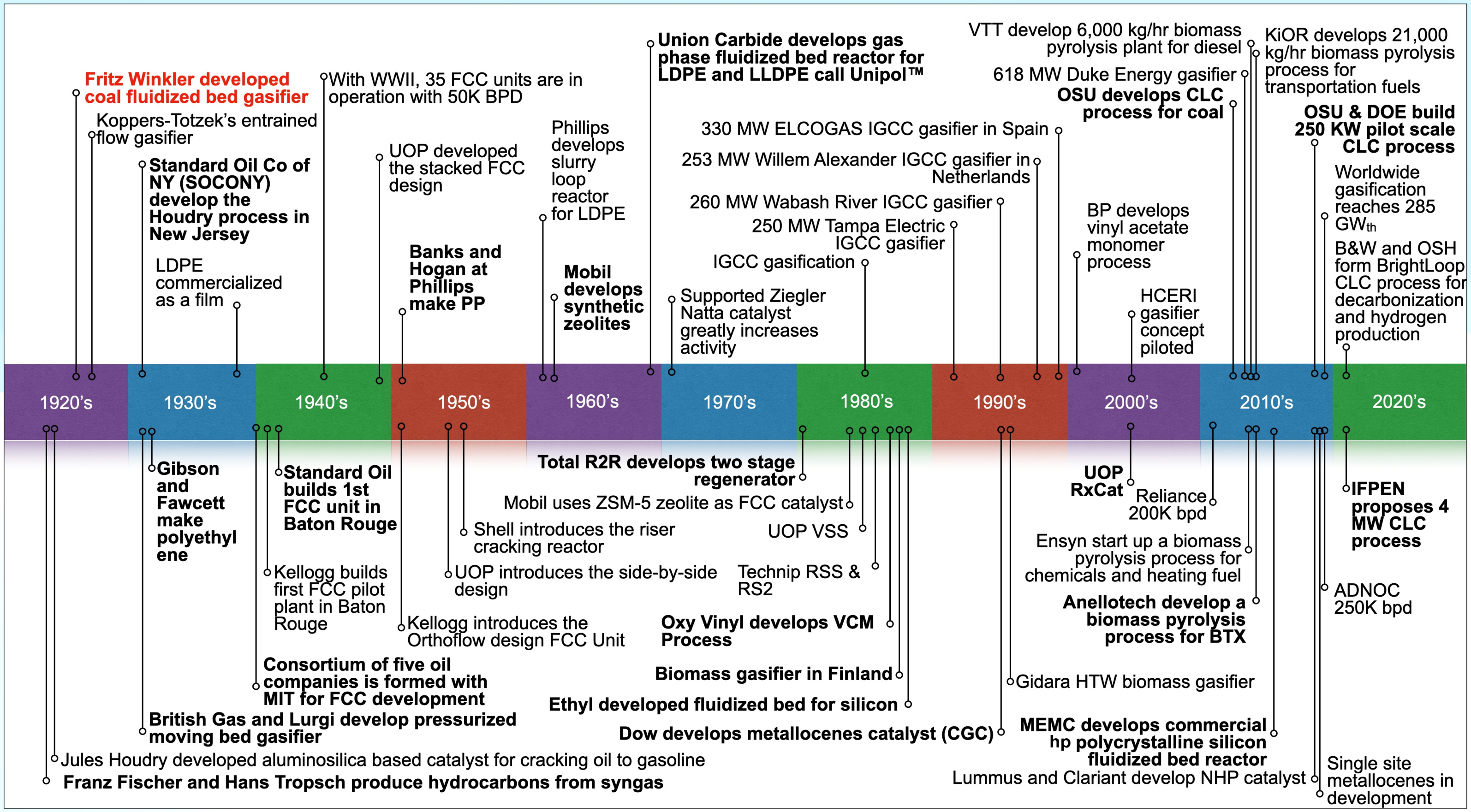
Jia Wei Chew, Wyatt LaMarche, Ray Cocco

2023 NETL Virtual Workshop on Multiphase Flow Science
Experimental Methods in Multiphase Flow
Aug 1, 2023; 1.40 – 2.00 pm ET, 12.40 – 1.00 pm CT

Chew, LaMarche, Cocco, 100 years of scaling up fluidized bed and circulating fluidized bed reactors, Powder Technology 409 (2022) 117813

2022: 100th year anniversary of the commercial fluidized bed

- 100 years of scaling up / optimizing: ↓ time to market, ↓ cost
- Why did fluidized bed become the breakthrough technology?



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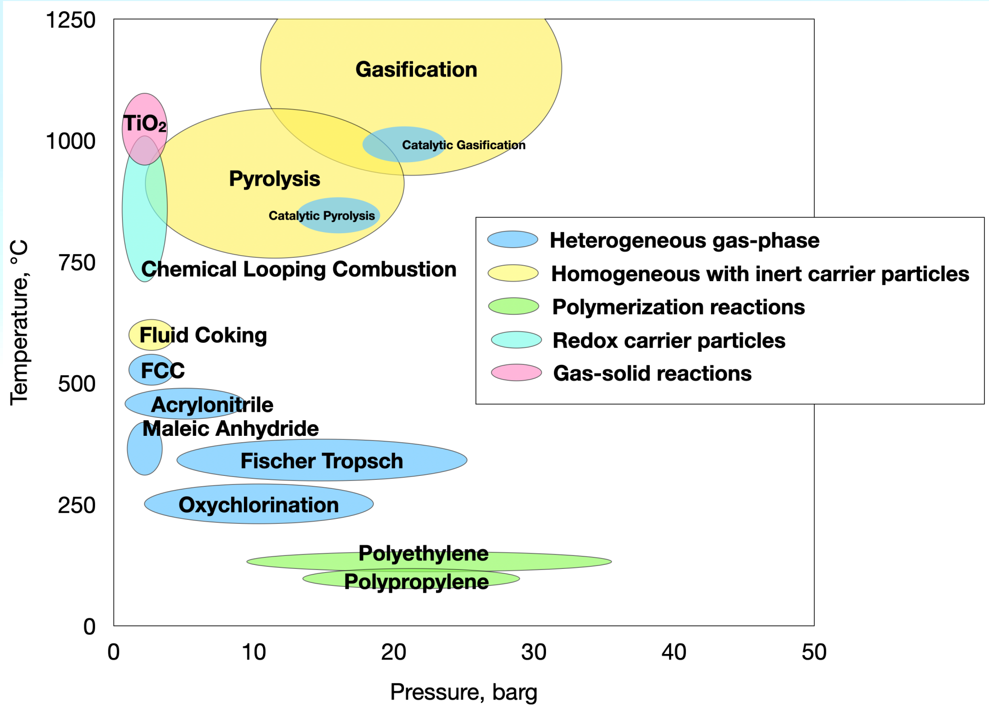
Applications of Fluidized Bed Reactors

- Fluidization has diverse applications in several key chemical reaction pathways
  - They all focus on **heat control** or **moving solids** or both
  - All of these processes are considered **breakthrough** processes that disrupted the conventional practice
- Despite the added complexity, there are a lot of high-pressure and/or high-temperature fluidized bed applications



Some Other Commercial Fluidized Bed Reactors

This list continues to grow with new applications in energy transition, sustainability, circularity, …

- Biomass pyrolysis
- Plastic pyrolysis
- Graphene production for batteries
- Methane decomposition for hydrogen
- Etc.

Application	Unit Operation	Industry	Approximate Commercialization
Acrylonitrile	Fluidized Bed	Chemicals	SOHIO in 1959
Biomass Gasification	Fluidized Bed	Petrochemical, Chemical	
Biomass Pyrolysis	Fluidized Bed	Petrochemical	Ensyn in 1989
Catalytic Oxidation (CatOx)	Fluidized Bed	Chemical	
Chemical Looping (Gas Feeds)	Circulating Fluidized Bed	Energy	
Chemical Looping (Coal Feeds)	Moving Bed	Energy	OSU/B&W Pending
Coal Gasification (Winkler)	Fluidized Bed	Petrochemical	BASF in 1921
Combustion (BFB)	Fluidized Bed	Energy	Foster Wheeler in 1977
Combustion (CFB)	Circulating Fluidized Bed	Energy	Foster Wheeler in 1981
Fischer Tropsch (Hydrocol)	Fluidized Bed	Chemicals	1946
Fischer Tropsch (Synthol)	Circulating Fluidized Bed	Petrochemcial	SASOL in 1955
Fluid Coke	Tandem Fluidized Beds	Petrochemical	ExxonMobile in 1958
Fluidized Catalytic Cracking (FCC)	Circulating Fluidized Bed	Petrochemical	Standard Oil of New Jersey in 1942
Hydrogen Chloride (HCl)	Tandem Fluidized Beds	Chemicals	Arad in 1960
Iron Ore Roasting	Fluidized Bed	Mining	BASF in 1953
Maleic Anydride (FBR)	Fluidized Bed	Chemicals	Mitsubishi in 1970
Maleic Anhydride (CFB)	Circulating Fluidized Bed	Chemicals	DuPont in 1996
Methane to Olefins (MTO)	Fluidized Bed	Petrochemical	UOP Honeywell/Norsk Hydryo in 1995
Methane Pyrolysis (Decarbinization)	Fluidized Bed	Energy	Pending
Phthalic Anhydride	Fluidized Bed	Chemicals	Sherwin Williams in 1928
Plastic Pyrolysis	Fluidized Bed	Petrochemical	
Polycrystalline Silicon	Fluidized Bed	Electronics	Ethyl in 1989
Polyethylene (Unipol)	Fluidized Bed	Chemicals	Union Carbide in 1968
Propane Dehydrogenation (FCDh)	Circulating Fluidized Bed	Chemicals	Dow, Pending
Titanium Dioxide	Fluidized Bed	Pigments	
Uranium Purification	Fluidized Bed	Mining	
Vinyl Acetate Monomer (VAM)	Fluidized Bed	Chemicals	BP in 2001
Vinyl Chloride Monomer (Oxychlorination)	Fluidized Bed	Petrochemical	Oxy Vinyls in 1986

Outline

- **100 Years of Commercial Fluidization**
  - The Early Years (1650’s – 1930’s)
  - The Renaissance (1940’s – 1990’s)
  - Today (2000’s – 2020’s)
  - Tomorrow

- **100 Years of Scale-Up**
  - Challenges
  - Historical procedures
  - Today
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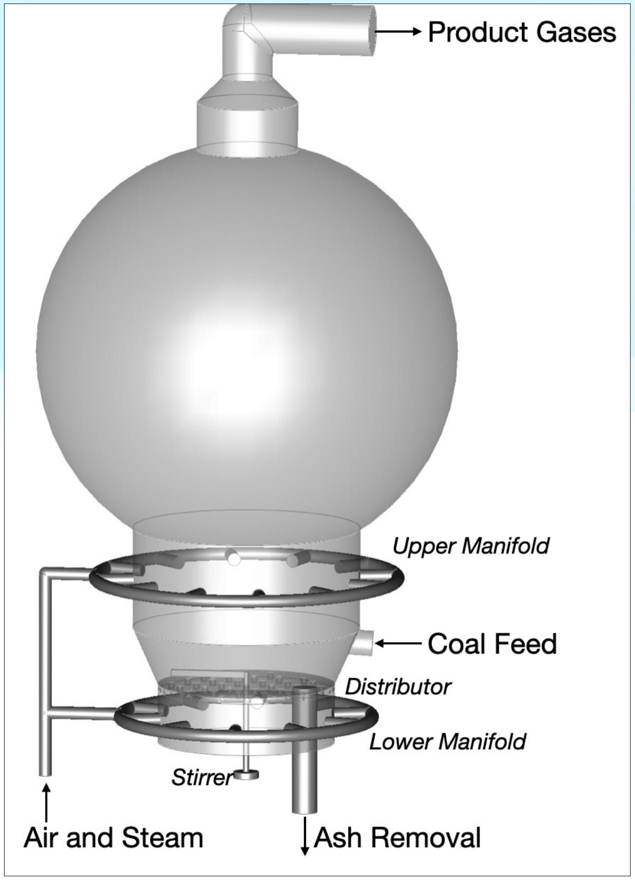
Winkler Gasifier

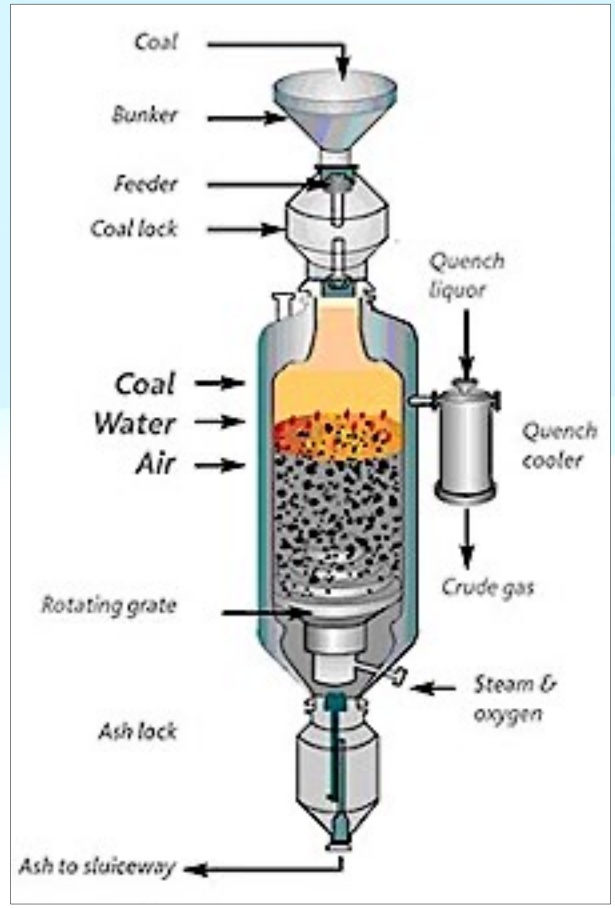
- December 1921 at BASF: Fritz Winkler mirrored his knowledge of the motion of boiling fluids to invent the first successful fluidized bed.
- Focus was on coal gasification
  - Hydrogen for BASF's ammonia plant and liquid fuels.
- Key advantages over the traditional gasifiers
  - Good mixing: Co-mixing coal with carbonized zinc chloride allowed for sulfur removal, a contaminant for the hydrogen stream.
  - Excellent heat transfer
  - Ability to add coal and remove ash



O. Levenspiel, What will come after petroleum? Ind. Eng. Chem. Res. 44 (2005) 5073–5078.

Lurgi Gasifier

- Commercialized in 1936 in Germany
- First large-scale CFB: cyclone, loop seal, heat recovery coil
    - High throughput: 15 times increase in capacity
- Operated at higher pressures 350 to 450 psi which provided higher methane yields
    - Feeder incorporated a lock hopper
- Coal feed particle size needed to be controlled, more so than the Winkler process
- Typically about 3.7 to 4.9 m (12 - 15 ft) in diameter
- 1950s: SASOL bought rights to Lurgi process



J. Werther, E.-U. Hartge, S. Heinrich, Fluidized-bed reactors–status and some development perspectives, Che. Ingen. Tech. 86 (2014) (2014) 2022–2038.

Fluidization: The Early Years

How We Got Here

1650's

Thomas Shirley discovers gas from coal mines

1700's

Dean Clayton distills coal in closed vessel

1750's

Felice Fontana discovers water gas shift reaction

First gasification patent by Robert Gardner

Coal gas for town gas used for lighting

1800's

France develops first gasifier

1850's

First US refinery in Pittsburgh as a one-barrel still, starts replacing whale oil

First internal combustion automobile is created in Germany by Karl Benz

Siemens develops commercial gasifier

John D. Rockefeller finances his first refinery

1900's

1910's

Friedrich Bergius develops coal liquifaction

Carl von Linde develops air separation

1920's

Franz Fischer and Hans Tropsch produce hydrocarbons from syngas

Jules Houdry developed aluminosilica based catalyst for cracking oil to gasoline

Fritz Winkler developed coal fluidized bed gasifier

Koppers-Totzek's entrained flow gasifier

1930's

Standard Oil Co of NY (SOCONY) develop the Houdry process in New Jersey

British Gas and Lurgi develop pressurized moving bed gasifier

Gibson and Fawcett make polyethylene

LDPE commercialized as a film

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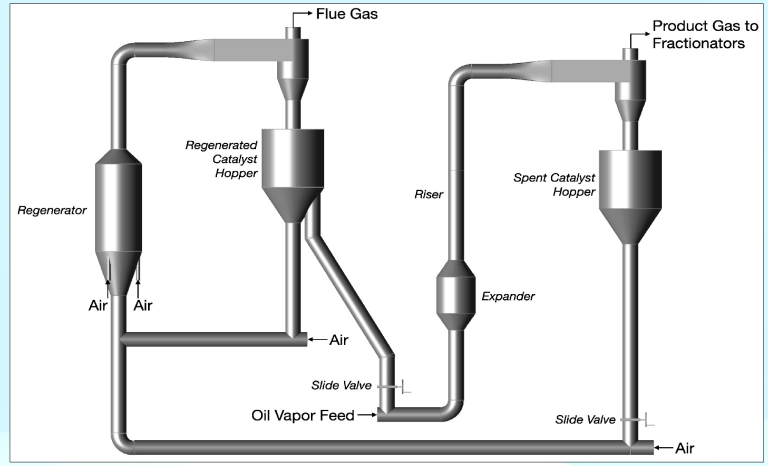
Fluidized Catalytic Cracking

- In 1920, Eugene Jules Houdry introduced catalytic cracking of oil which provided significant yield improvements over thermal cracking
  - However, the catalyst deactivated quickly
- In 1940, the US formed the Catalytic Research Association (CRA) consisting of Standard Oil, Kellogg, Anglo-Iranian, Shell, Texaco, and UOP
- CFB developed for petroleum cracking
  - Pilot facility build in 1941
  - Full scale operational in 1942
  - By 1945, there were 35 operational FCC units in the US



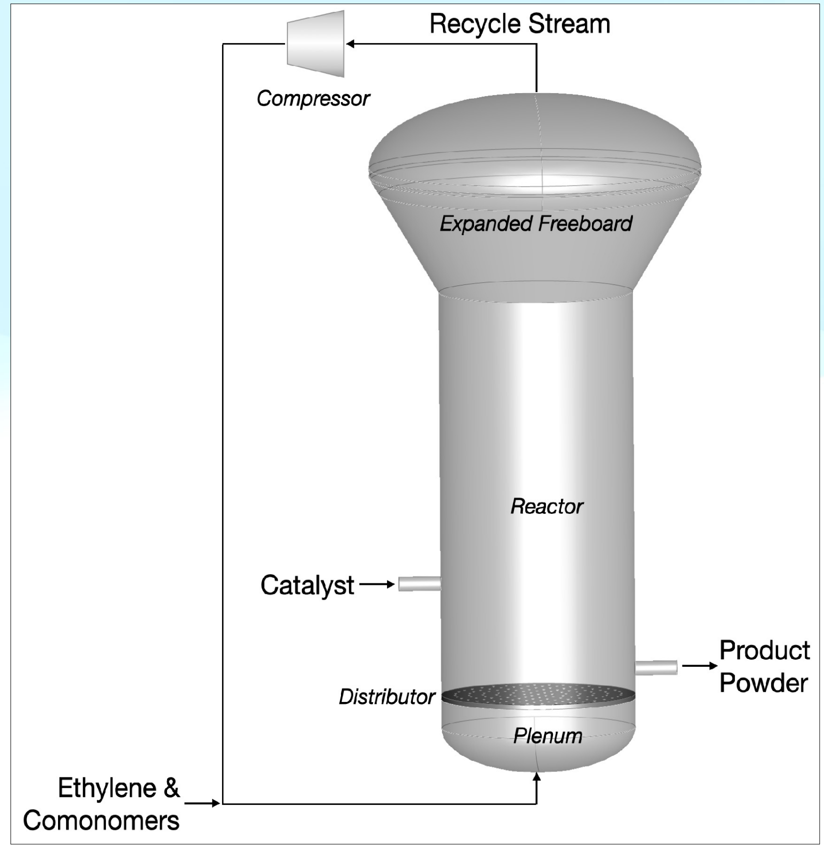
Standard Oil Company Model 1 FCC unit.

A. Avidan, R. Shinnar, Development of catalytic cracking technology. A lesson in chemical rector design, Industrial & Engineering Chemistry Research 29 (1990) 931-942.

Standard Oil Company Model 1 FCC unit in Baton Rouge, LA.

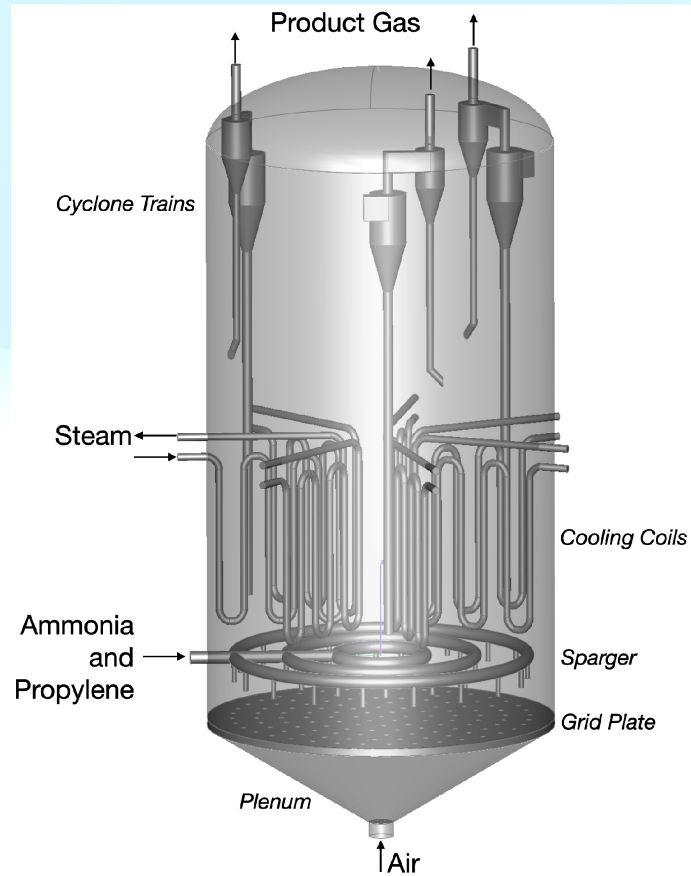
Polyolefins

- 1890's: Production of Polyolefins started but was difficult
- 1938: 1st polyethylene plant but operation was expensive
- 1950: Catalytic polymerization was developed and production of polyethylene using autoclave reactors (3-130 barg) started
  - 1957: Polypropylene started
- 1961: Dow developed the loop reactor that was the breakthrough for commercial production (↓ cost by 75%)
  - Issues with scale-up, broad MW distributions
- 1968: Union Carbide developed the gas-phase fluidized bed polymerization reactor called Unipol
- 1989: Constrained-geometry catalyst developed for LLDPE and the fluidized bed reactor was a perfect fit
- 2018: 40% of the polyethylene production is made via fluidized beds (Unipol, Spherilene, Innovene designs)



Acrylonitrile

- 1930: Acrylonitrile was commercialized in Germany for synthetic rubber
  - Multi-step, highly-exothermic reactions and the “fuel” air mixture was prone to runaways
- 1940: Alternative reaction route – single-step propylene ammoxidation
- 1960: SOHIO developed the catalytic ammoxidation process
  - High heat of reaction managed using a fluidized bed
  - Today, 90% of acrylonitrile produced via Sohio



Fluidization: The Renaissance

How We Got Here

1940's

- With WWII, 35 FCC units are in operation with 50K BPD
- UOP developed the stacked FCC design
- **Standard Oil builds 1st FCC unit in Baton Rouge**
- Kellogg builds first FCC pilot plant in Baton Rouge
- **Consortium of five oil companies is formed with MIT for FCC development**

1950's

- **Banks and Hogan at Phillips make PP**
- Kellogg introduces the Orthoflow design FCC Unit
- UOP introduces the side-by-side design
- Shell introduces the riser cracking reactor

1960's

- Phillips develops slurry loop reactor for LDPE
- **Mobil develops synthetic zeolites**
- **Union Carbide develops gas phase fluidized bed reactor for LDPE and LLDPE call Unipol™**

1970's

- Supported Ziegler Natta catalyst greatly increases activity

1980's

- IGCC gasification
- 250 MW Tampa Electric IGCC gasifier
- **Total R2R develops two stage regenerator**
- Mobil uses ZSM-5 zeolite as FCC catalyst
- UOP VSS
- Technip RSS & RS2
- **Oxy Vinyl develops VCM Process**
- **Biomass gasifier in Finland**

1990's

- 260 MW Wabash River IGCC gasifier
- 253 MW Willem Alexander IGCC gasifier in Netherlands
- **330 MW** ELCOGAS IGCC gasifier in Spain
- **Dow develops metallocenes catalyst (CGC)**
- Gidara HTW biomass gasifer

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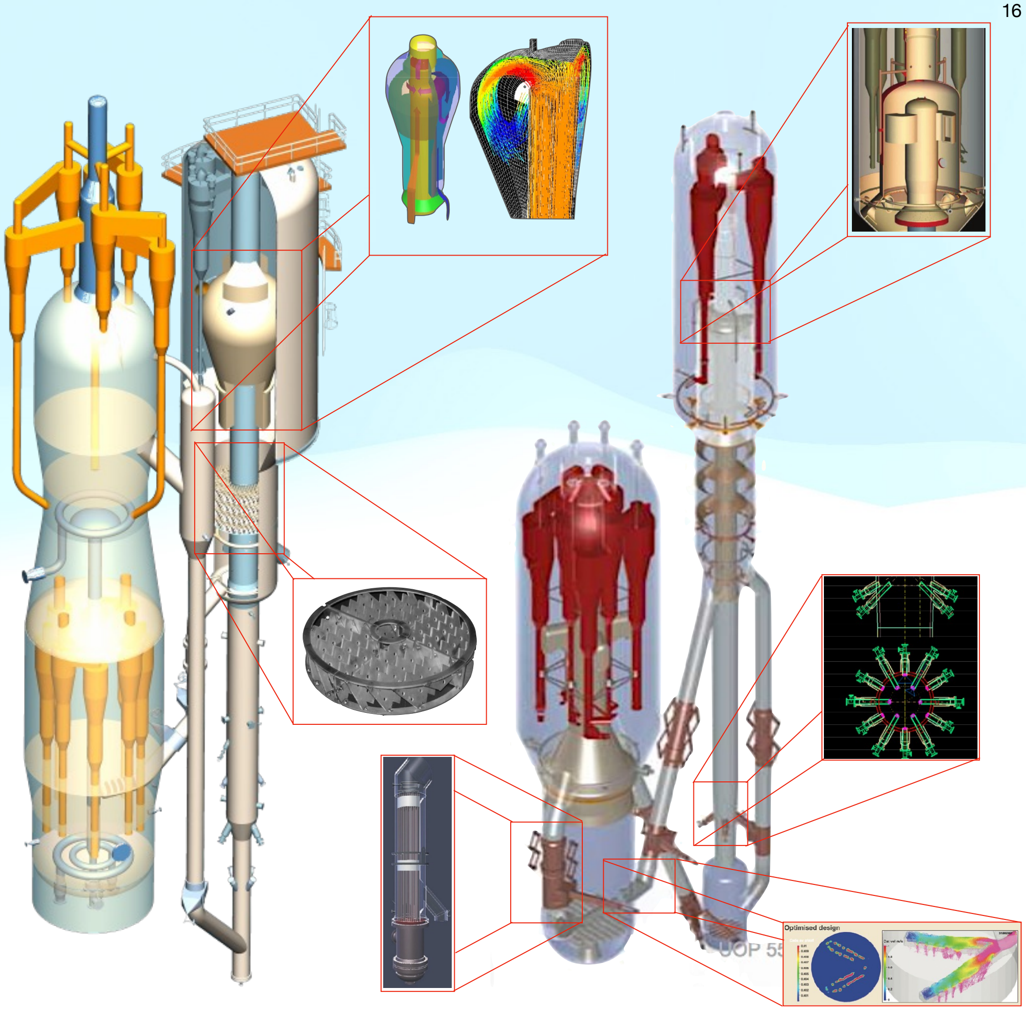
Fluidization: Today

Modern FCCs

- Two regenerators in series provides better flexibility with temperature and thus managing delta coke levels
  - Catalyst coolers and RxCat riser recycling stream **decouple solids circulation and energy circulation**, providing an even higher level of flexibility
- Structured packing from static mixers leveraged as stripper elements
- R2R or VSS riser terminators provide quick gas-solid disengagement while minimizing particle attrition



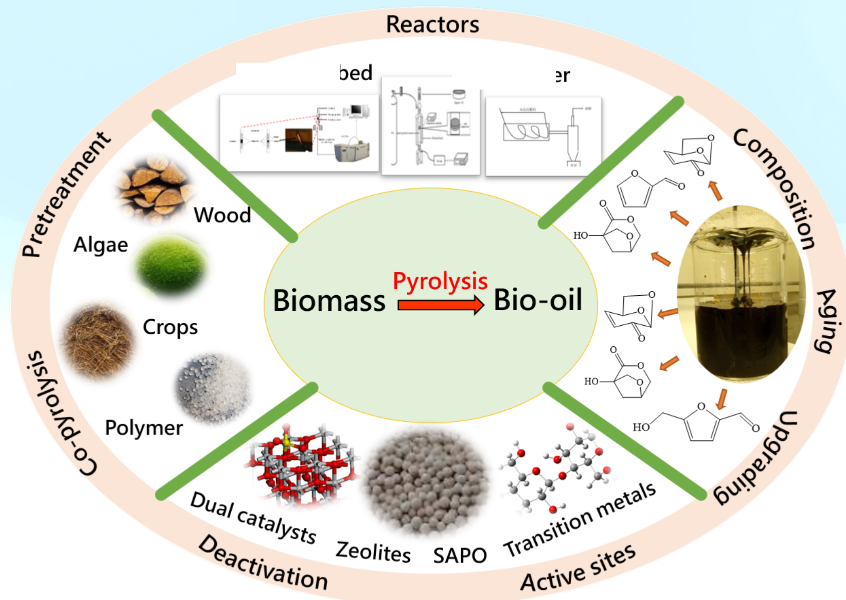
Technip Stone & Webster R2R

UOP RxCat with VSS

Paolo Palmas, FCC and 25 years of development, Hydrocarbon Engineering, June 2009

Pyrolysis

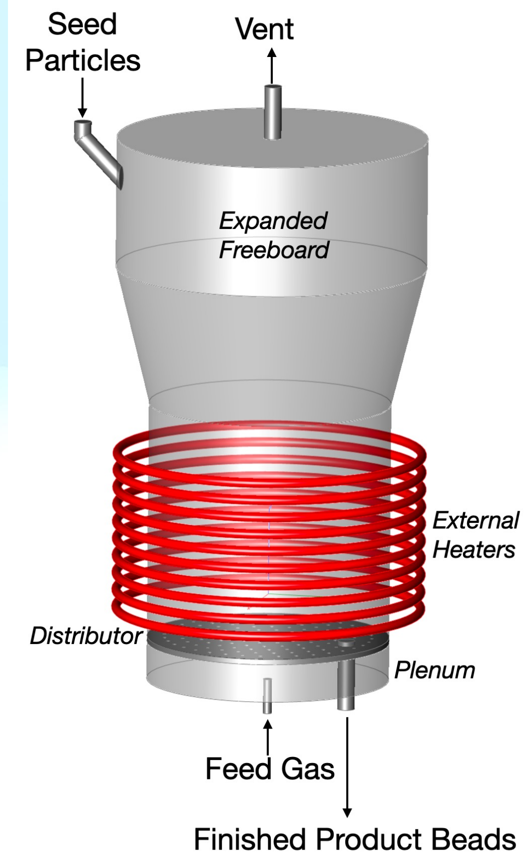
- Fast pyrolysis has limitations
  - Tars
  - Oxygenates
- Catalytic pyrolysis addresses these limitation
- Feedstocks now vary from wood (traditional) to algae, crops, and polymers (future)
- Product lines include bio-oils and upgrades to diesel, BTX, heating fuels, and aliphatic oils
- Coming soon … methane pyrolysis



L. Zhang, et al., Catalysts **2018**, 8(12), 659

Polycrystalline Silicon

- 1950s: Siemens CVD process
- 1987: Ethyl CVD route in a fluidized bed
  - Silane decomposed to polysilicon particles of high purity
  - First commercial fluidized bed polysilicon production
  - REC, Wächer, Hemlock Semiconductor, etc. followed suit
- 2011: Samsung-MEMC initiated new high-pressure fluidized bed reactors (HP-FBRs)



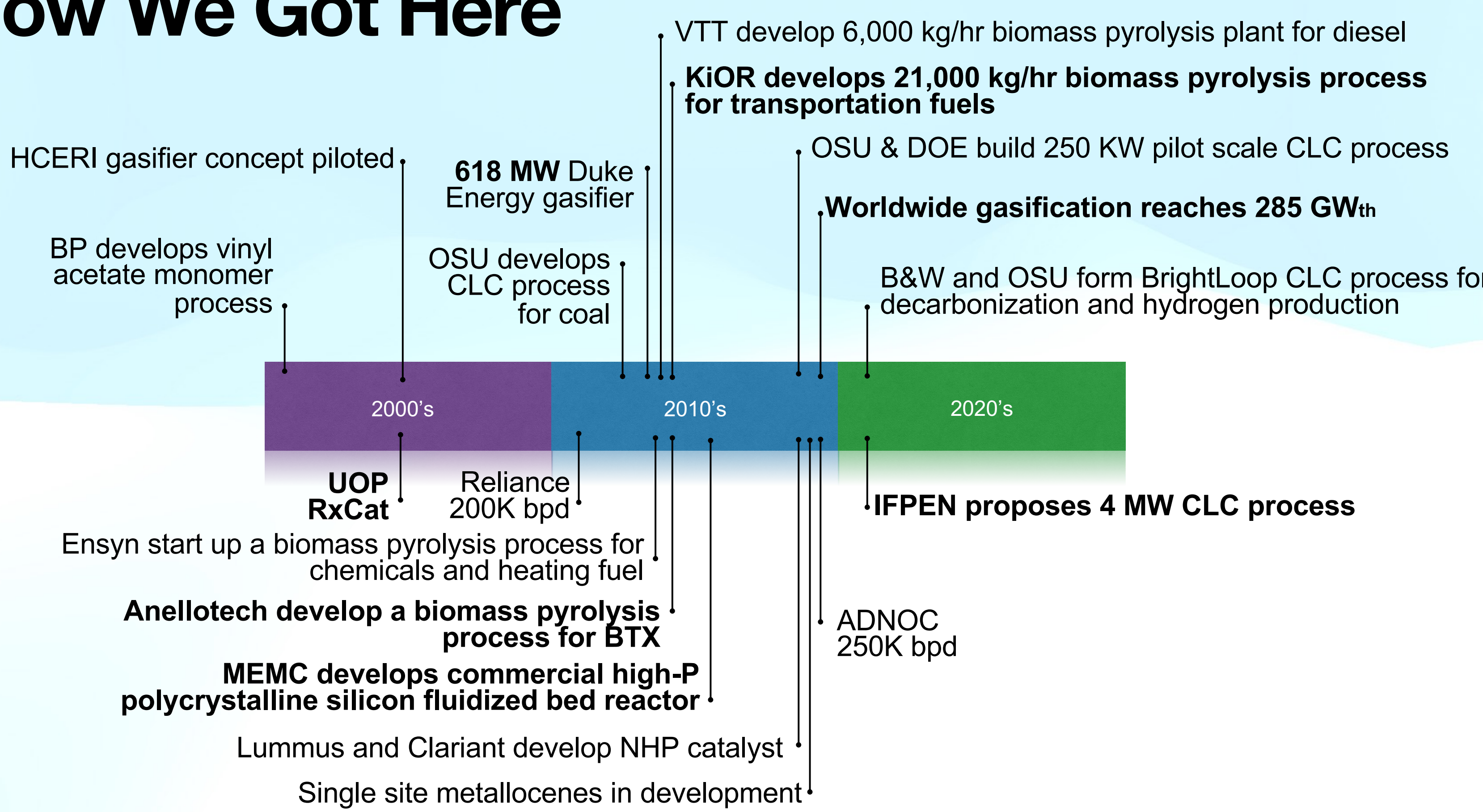
Chemical Looping

- Proposed in the 1990's
  - Butane dehydrogenation with Dow
  - Maleic anhydride with DuPont
- Being developed for
  - Natural gas combustion in Europe
  - Hydrogen production from coal, biomass, and methane
  - Carbon capture

DOE Pilot Scale Demonstration Unti

C. Chung, L.S. Fan, Iron-based chemical looping processes, CO2 Summit II: Technology and Opportunities, ECI Digital Archives, May 4, 2016

How We Got Here



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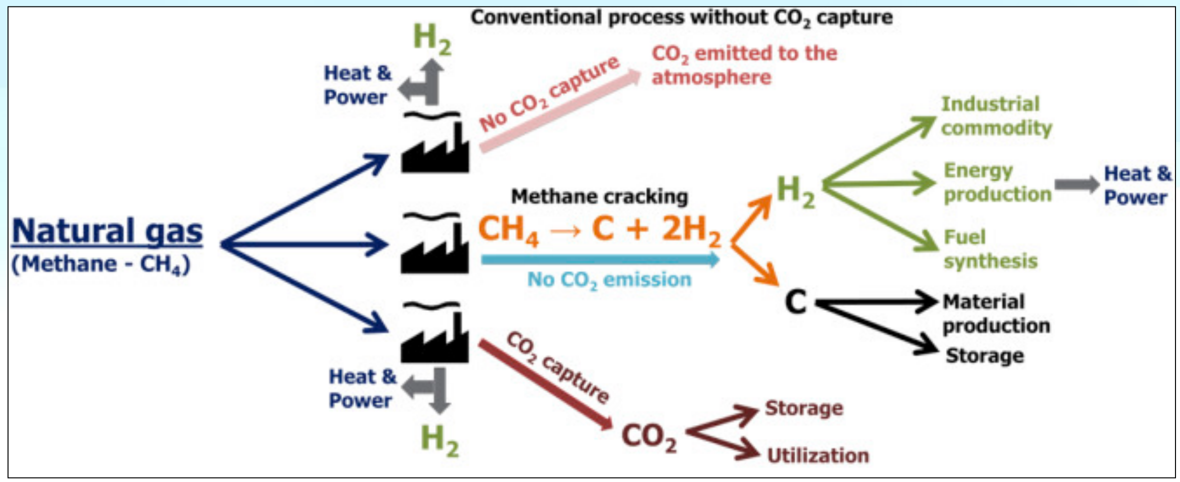
Where We Are Going?

- Sustainability, renewable energy, green chemicals, circularity…
  - Biomass pyrolysis
  - Plastic pyrolysis
  - Methane decarbonization
  - Ethane and propane dehydrogenation
  - Graphene production for batteries
  - Carbon capture
  - Etc.



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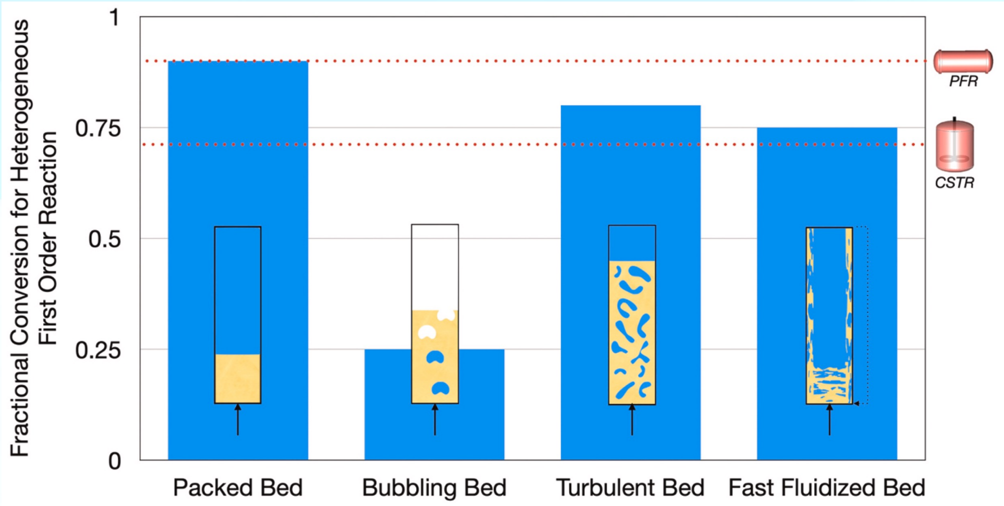
Scale-Up Challenges

- Solids losses: attrition, entrainment rates, cyclones
- Representative scale: bubbles, bed density
- Hydrodynamics: fluidization regime, Geldart group, mass transfer, back-mixing



Historical Scale-Up Procedures

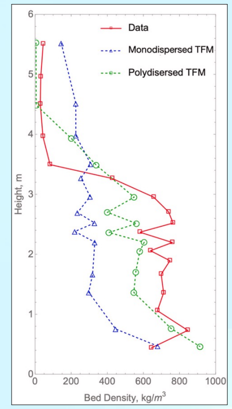
- Trial and error

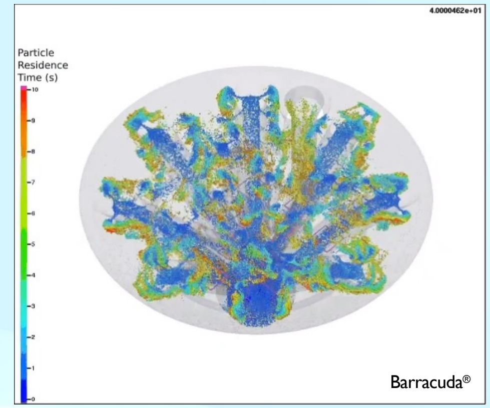
- When PFRs and CSTRs scaled at 1,000 to 10,000 times,
  - 1940s: FCC scaled at factors of 20 – 150 times from pilot- to commercial-scale
  - 1950s: Fluid coking scaled at 37 times from pilot- to commercial-scale

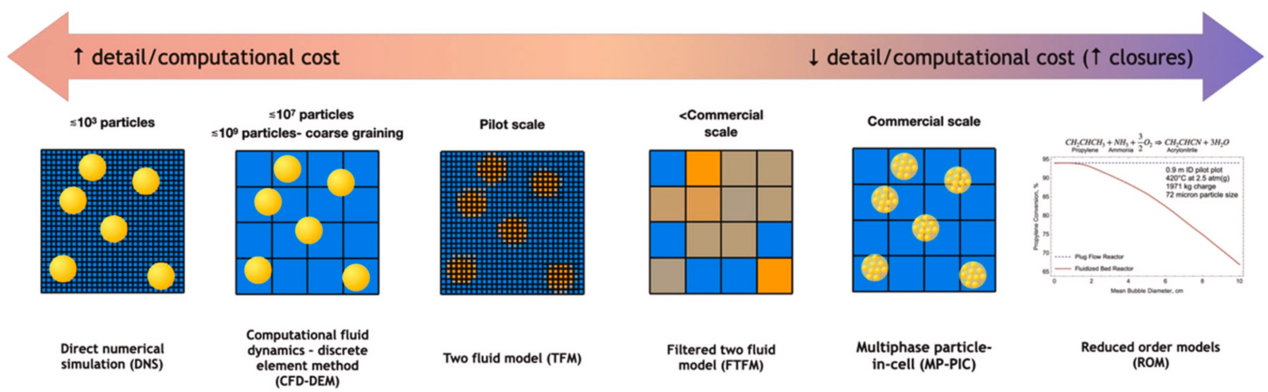
- Demand for faster, cheaper scale-up
  - 1960s: Bubble behavior, bed density
  - 1970,80s: TDH, entrainment rate, cyclone designs, jet penetration lengths
  - 1990s: Scaling laws, compartment models

Recent Scale-Up Procedures

- Eliminate one scale-up unit = savings of 3 years, $30 M
- CFD
  - Captures heterogeneous structures
  - Shortfalls: drag, particle size distribution
  - CFD-DEM, MP-PIC, DDPM
- PBM
  - Attrition: de-risk particle loss
- Experiments
  - Proof of concept, validation data for CFD, unexpected behaviors, risk mitigation
  - More emphasis on particle properties as applied to hydrodynamics







Tomorrow's Scale-Up Procedures

- Late 1990s: US DOE's Vision 2020 of scale-up using computations
- **Improved experiments**
  - More insights through better probes, better data-analysis
- **Improved models**
  - Increased CPU/GPU speeds and memory architecture
- **Machine-learning / artificial intelligence**
  - Data-driven models for mechanistic understanding and predictive capability
  - Hybrid CFD-NN models
- **AI-driven optimization**
  - Equipment design
  - Flow sheet design

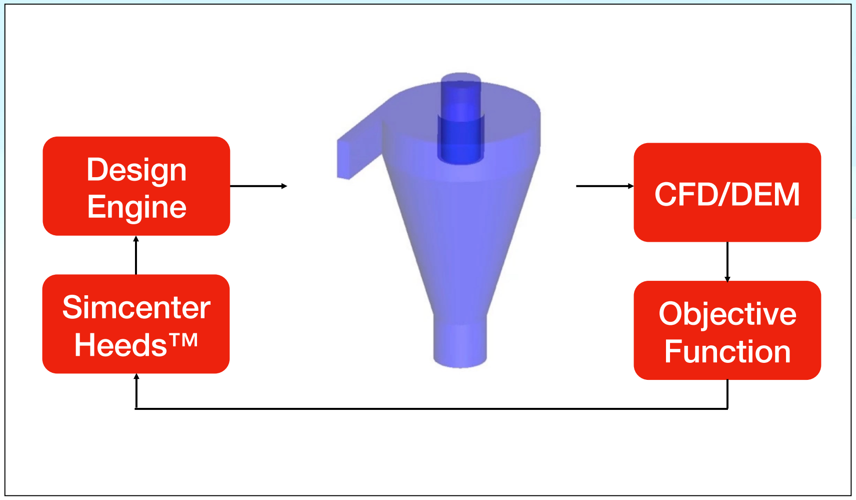


Illustration of AI-Driven Equipment Design

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Summary

The History of Commercial Fluidization

- Fluidized reactors have been responsible for a lot of breakthrough technologies
- Expect more breakthroughs

1st 80 years was pretty much Edisonian or stochastic

Renaissance era moved us towards a deterministic discipline

With ML/AI, future likely a hybrid of stochastic & deterministic

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