

The Eight Steps to Specify a Catalyst Bed

Gary Gildert for the East Tennessee Local Section of the AIChE

November 4, 2014



Johnson Matthey
Process Technologies

Johnson Matthey

Overview

- A speciality chemicals company and a world leader in sustainable technologies
- Origins date back to 1817, floated 1942, FTSE 100 company since June 2002
- £11.2 billion revenue and underlying profit before tax* of £427.3 million for year ended 31st March 2014
- Operations in over 30 countries with around 12,000 employees
- Leading global market positions in all its major businesses

* Before amortisation of acquired intangibles, major impairment and restructuring charges and profit or loss on disposal of businesses and, where relevant, related tax effects.

Our Strategy

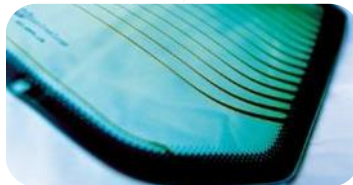
Technology leadership forms the basis of Johnson Matthey's strategy to deliver superior long term growth



Divisional Structure



Johnson Matthey



Emission Control Technologies

- Light Duty Catalysts
- Heavy Duty Catalysts
- Stationary Emissions Control

Process Technologies

- Chemicals**
 - JM Davy Technologies
 - Syngas
 - **Chemical Catalysts (inc. Formox)**
- Oil and Gas**
 - Refineries
 - Purification
 - Tracerco

Precious Metal Products

- Services**
 - Platinum Marketing and Distribution
 - Refining
- Manufacturing**
 - Noble Metals
 - Colour Technologies
 - Chemical Products

Fine Chemicals

- Active Pharmaceutical Ingredient (API) Manufacturing
- Catalysis and Chiral Technologies
- Research Chemicals

New Businesses

- New Business Development
- Water
- Battery Technologies
- Fuel Cells

Process Technologies

Chemicals

Formox

**Chemical
Catalysts**

Katalco SM
Activate your potential

Davy

Protelec

Tracerco 
Providing Insight Onsite

Oil & Gas

Katalco SM
Activate your potential

Puraspec SM

INTERCAT SM

Hytreat SM

Puracare SM

Tracerco 
Providing Insight Onsite

A global supplier of catalysts, licensing technologies and other services to the petrochemical, syngas, oil refining and gas processing industries.

Chemical Catalysts

Overview, Markets and Segments

- Fixed bed supported catalysts in base metals (e.g. Ni, Cu, Co, Zn) from Oberhausen, Emmerich (Germany) and Clitheroe (UK)
- Ni catalysts for edible oils & oleochemicals from Emmerich (Germany) and Taloja (India)
- Sponge Metal™ catalysts from Tennessee (USA)
- Supported precious metal catalysts from Royston (UK) and West Deptford (USA)

Petrochemicals



Olefins



Alcohols



Solvents and Fuels



Fluorochemicals



Chemical Intermediates



Environmental

Oleochemicals



Fatty Acids



Edible Oils



Polyols



Natural Detergent Alcohols



Biorenewables

Formaldehyde



FORMOX™ Fe/Mo catalysts



FORMOX™ Plant Technology

Custom Catalysts

Gary Gildert

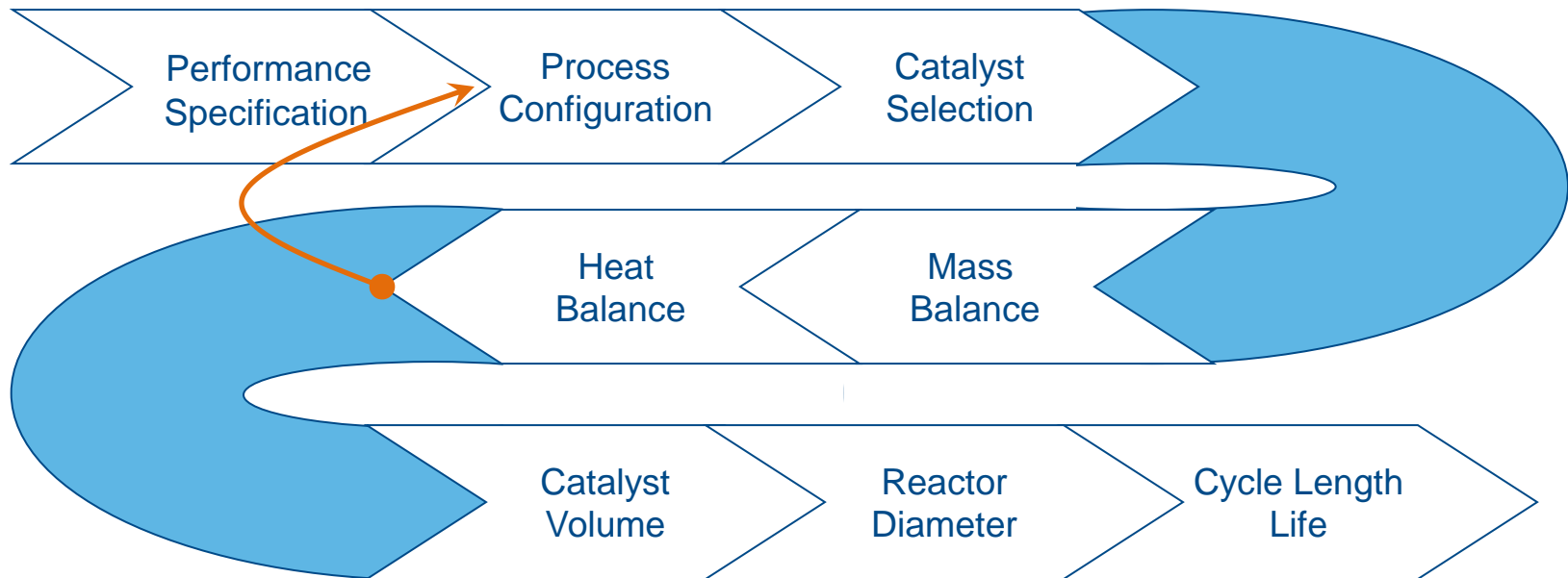
Internationally recognized expert in hydro treating with 24 patents and over 40 publications

- Bachelor of Applied Science (Ch.E.), University of Waterloo 1981
- Masters of Business Administration, Rice University in 2005
- Registered professional engineer in Ontario, Canada (1986) and Alberta, Canada (1990)
- Member of American Institute of Chemical Engineering since 1997, STS Chair 2013
- Member of American Chemical Society and South West Catalysis Society since 2005

Over 30 years of petrochemical knowledge including new process development and catalyst design and manufacture

- 11 years operations support and process design with Petrosar
- 8 years Process Development Manager Hydrogenation Technology at Chemical Research and Licensing (CDTECH) in Houston, TX.
- 6 years, Regional Sales Manager, Americas for catalysts including technical support globally for olefins purification catalysts
- Co-founder Custom Catalytic Solutions, responsible for marketing, sales, technical service, and finance.
- 5 years, Senior Principal Process Engineer, Johnson Matthey, Process Technologies with responsibilities for technical service, technical mentoring and marketing new hydrogenation catalysts.

The Eight Steps



1. Performance Specification

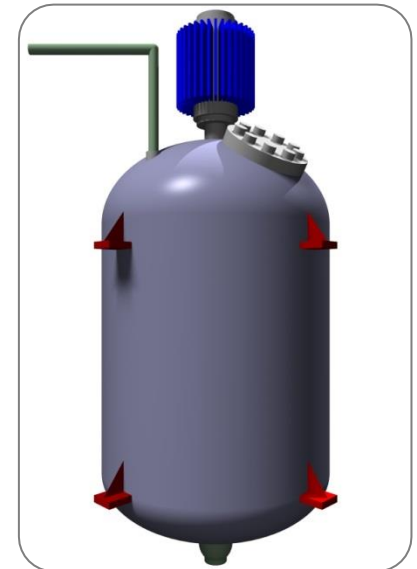
- Feed rate + margin
 - Maximum rate for sizing
 - Normal rate for life
- Stream properties
 - Hydraulics
 - Detailed composition, or
 - Actual density, viscosity (gas and liquid if 2-phase) , surface tension
- Key concentrations for bed sizing – feed and product.
 - Limiting reactant
 - Basis for specification
- Hydrogen source
 - Purity
 - Pressure
- Poisons
 - assumptions vs. history
- Alternate cases
 - One case governs sizing
 - Others do not affect result
- Units of measurement

Application Questionnaire

Application Information						
Acetylene Converter, Tail-end						
Company:					Date:	
Location:					By:	
Process Information						
De-ethanizer Overheads		Normal	Maximum	Feed Contaminants		
Feed rate	kg/hr			H ₂ S	ppm m	
Composition				COS	ppm m	
Methane	mol %			Arsine	ppb w	
Acetylene	mol %			water	ppm m	
Ethylene	mol %					
Ethane	mol %					
Propylene +	mol %					
Hydrogen Composition						
Hydrogen	mol %					
Methane	mol %					
Carbon Monoxide	mol %					
Ethane +	mol %					
Product Specification						
		Maximum	Typical			
Acetylene	ppm m					
Hydrogen	ppm m					

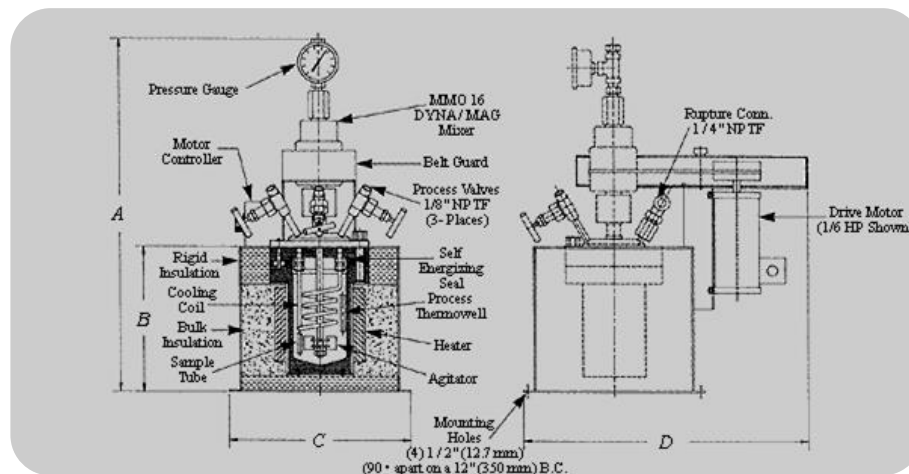
2. Process Configuration

- Batch Reactor
- Continuous Stirred Tank Reactor
- Plug Flow Reactor
 - Adiabatic
 - Isothermal
- Fluidized Bed



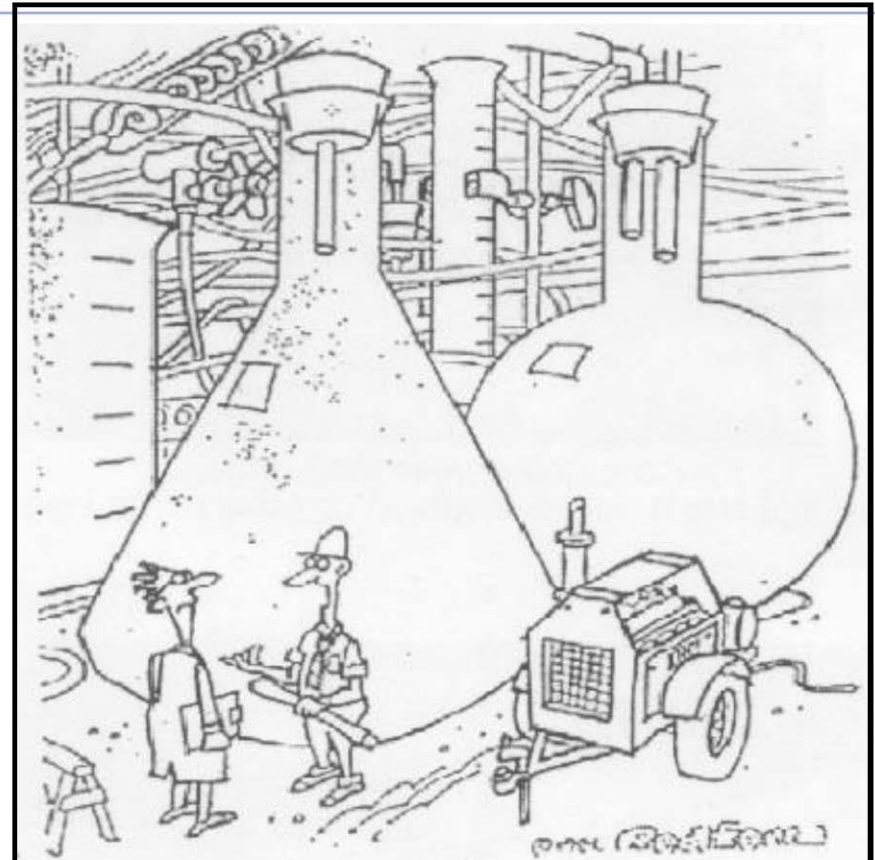
Configuration - Batch

- Discovery of most reaction chemistry (Chemists)
- Reusable powdered catalyst
- Easily reproduced
- Easy translation to (small) commercial scale



Batch Reactor

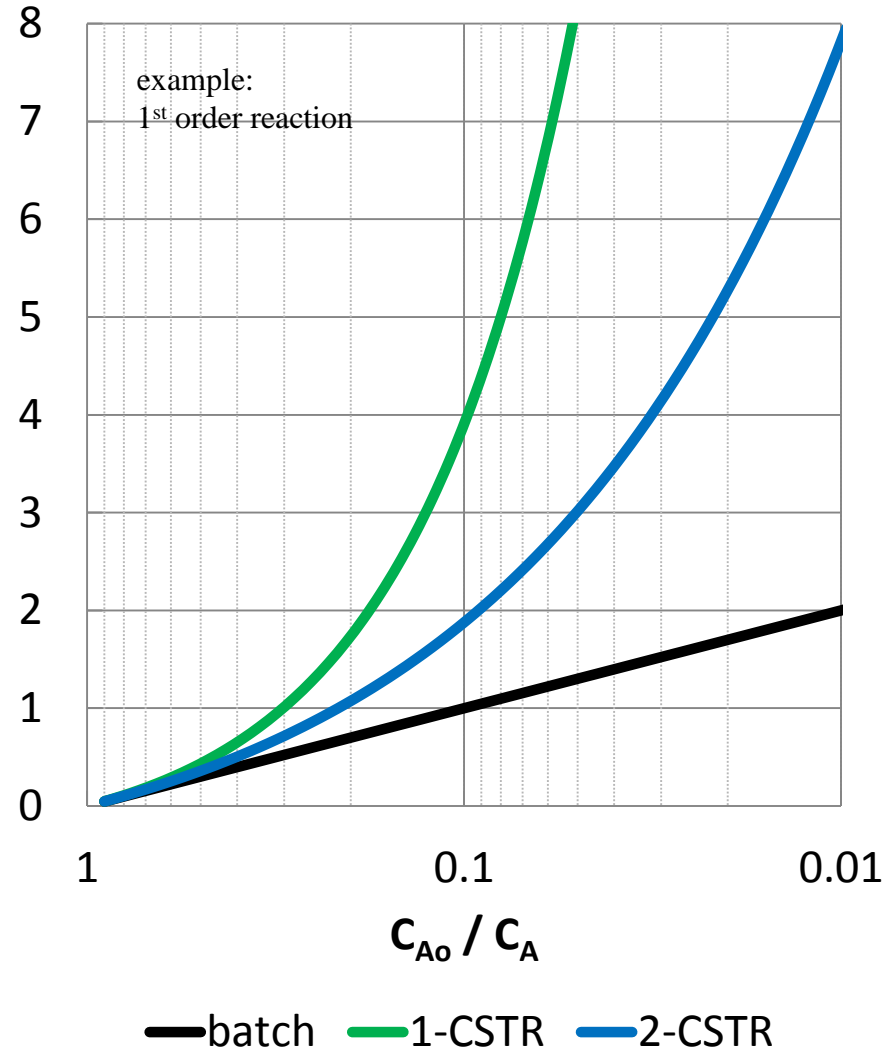
- Does not scale easily to large volumes
- Batch time = Fill time + reaction time + discharge time
- Catalyst active during product discharge
- Product heel



**We had a small problem with the scale-up
out of the laboratory....**

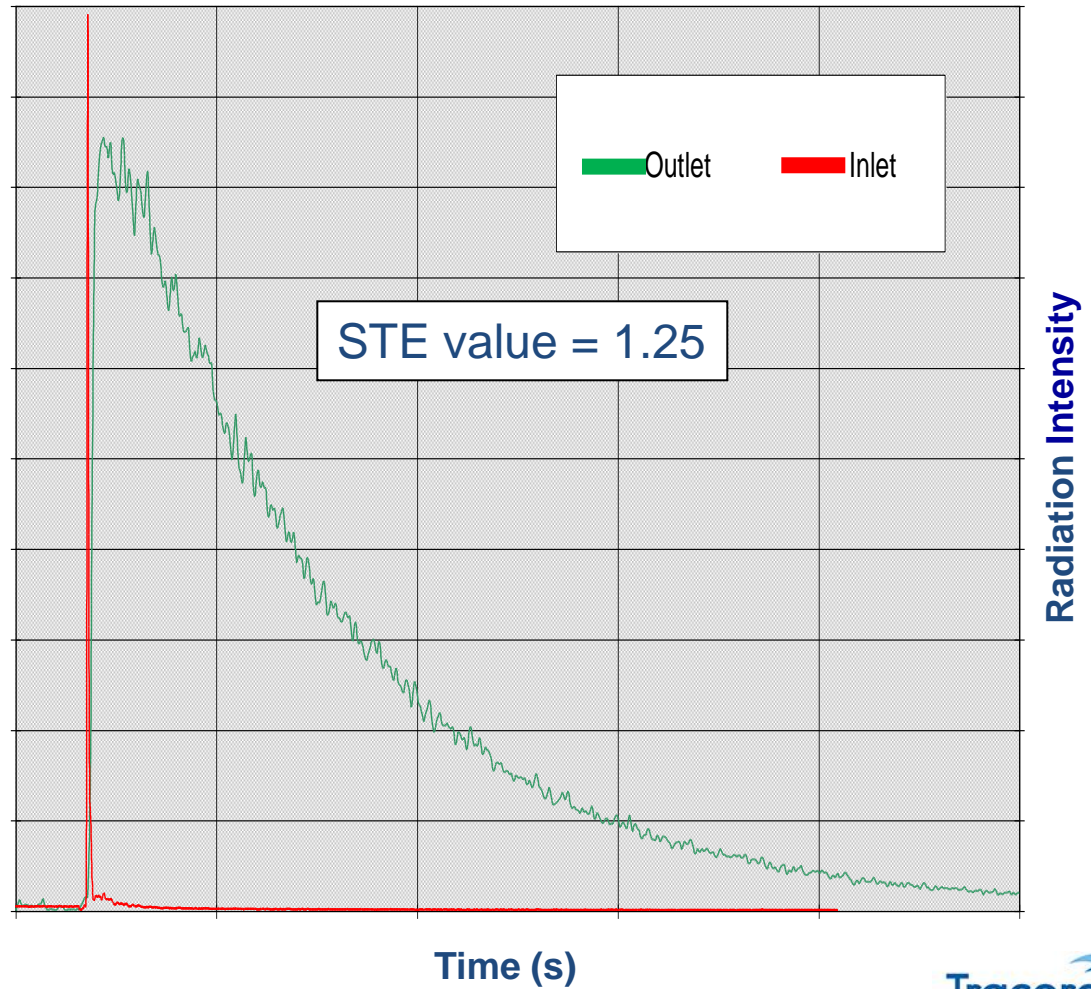
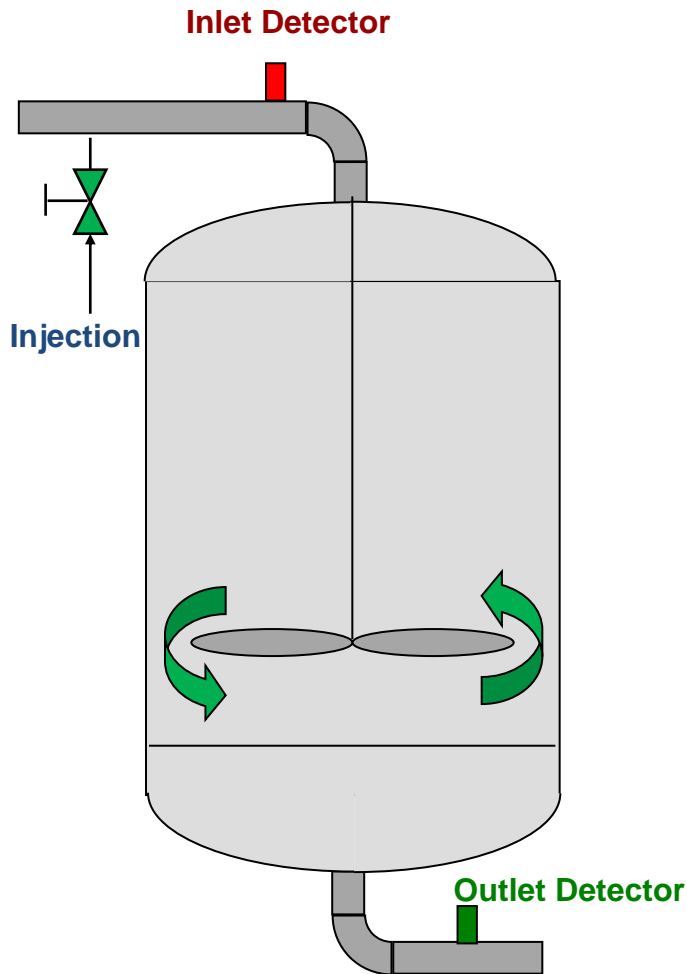
Configuration - CSTR

- Continuous flow
 - no fill time
 - no discharge time
 - no product heel
- Isothermal
- Low concentration
 - low fouling
 - Low reaction rate if higher order
- Higher contact time than batch?



TRACERCO Diagnostics™

Residence Time of Stirred Tank Reactor

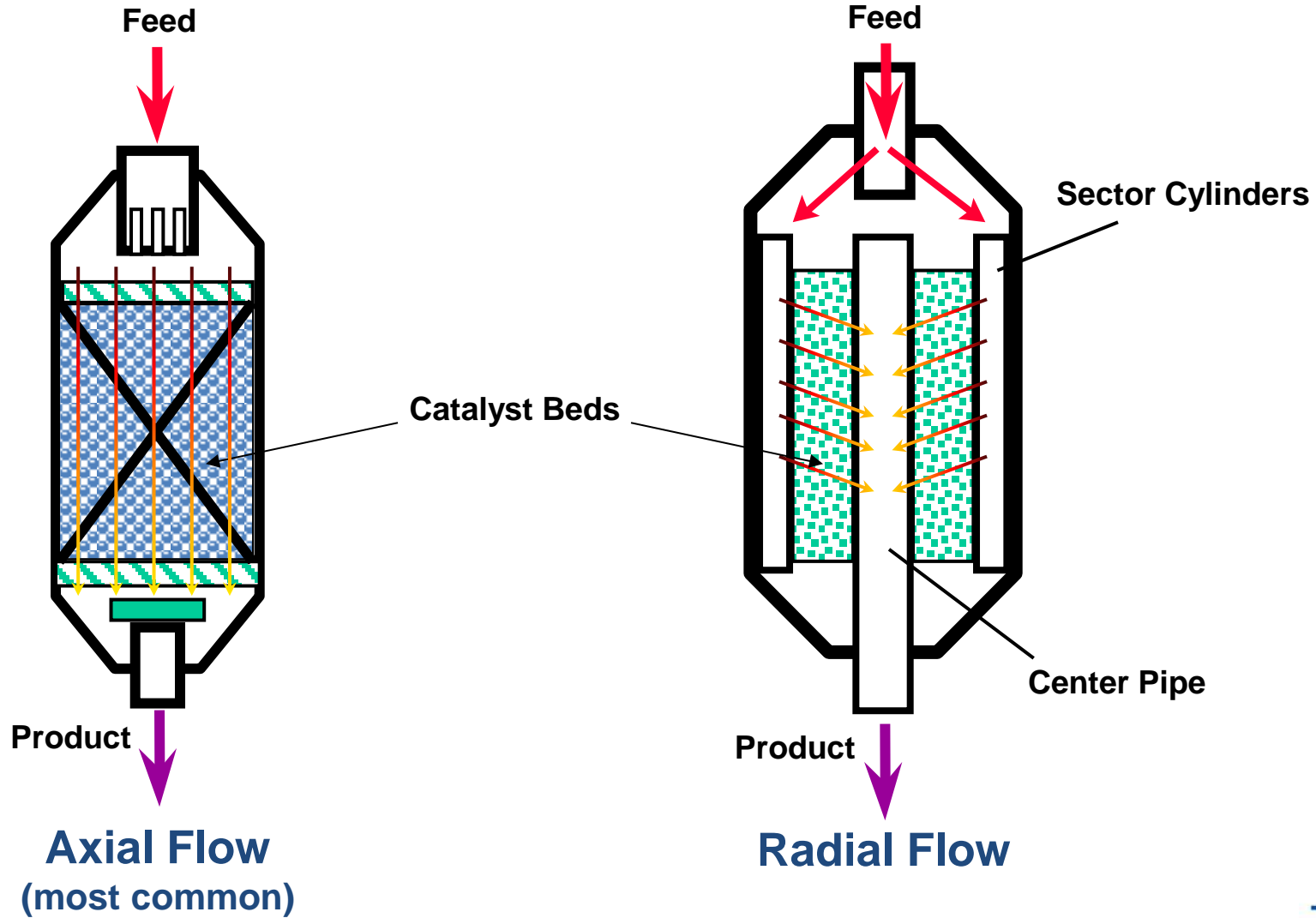


Configuration - PFR

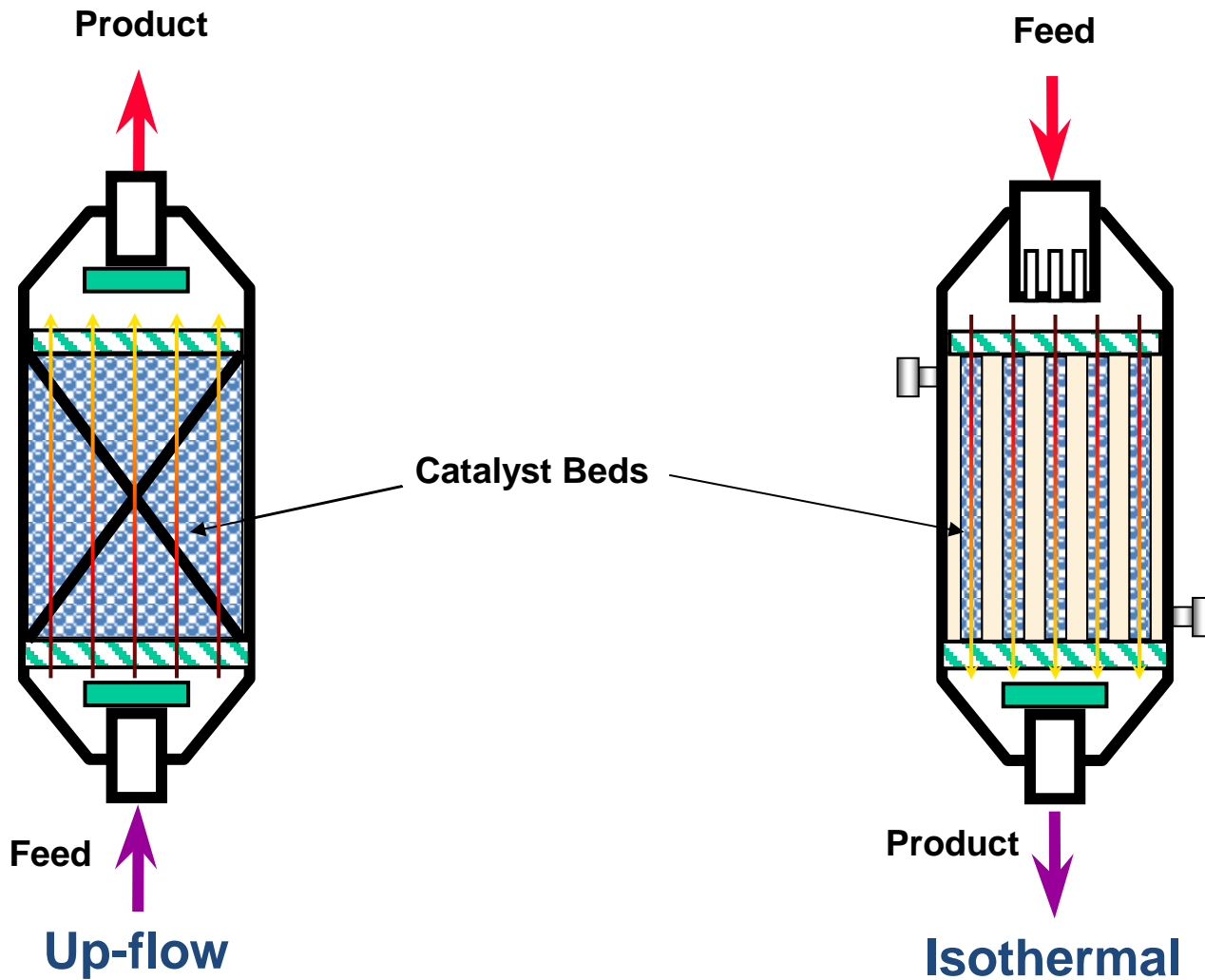
- Most Common Configuration
- Vapor Phase, Liquid Phase, Trickle Bed
- Many variations



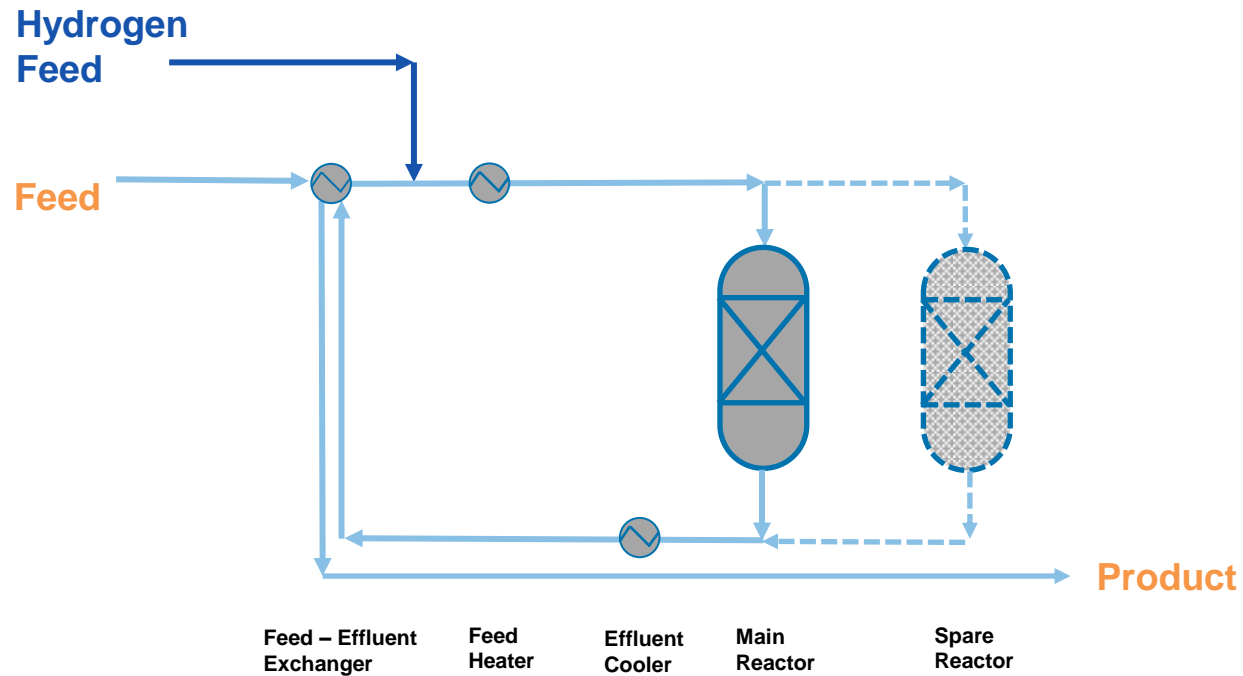
Two Reactor Designs



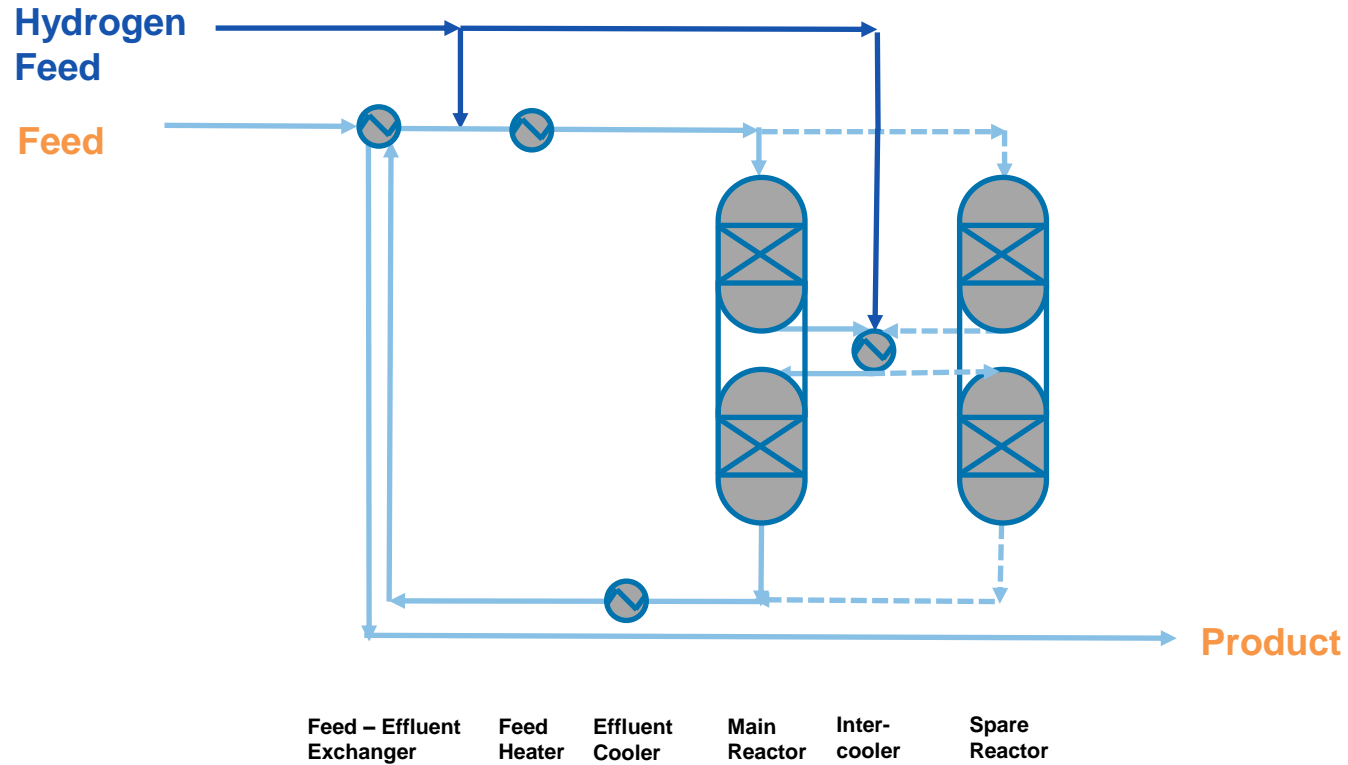
Two More Reactor Designs



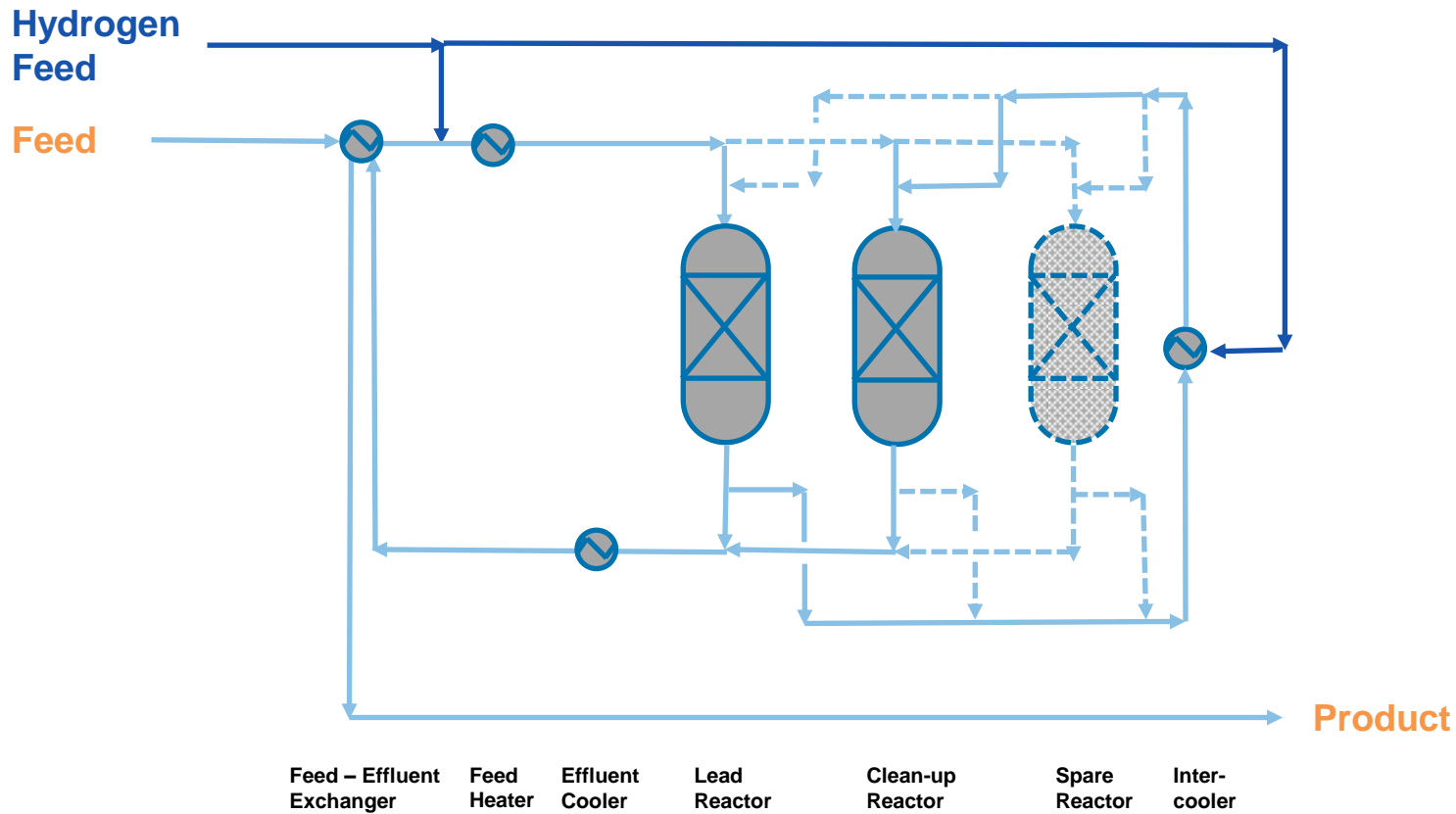
Single Bed Reactor with Spare



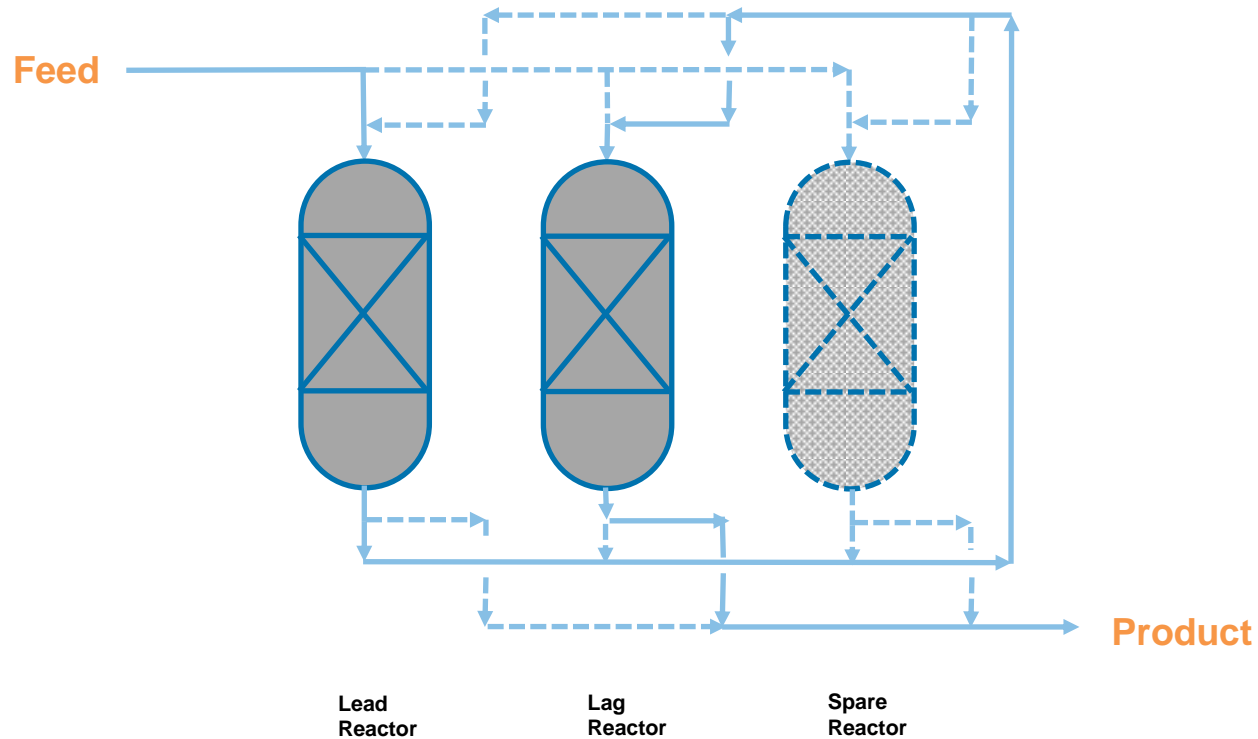
2 X 2 (Two in series with two spares)



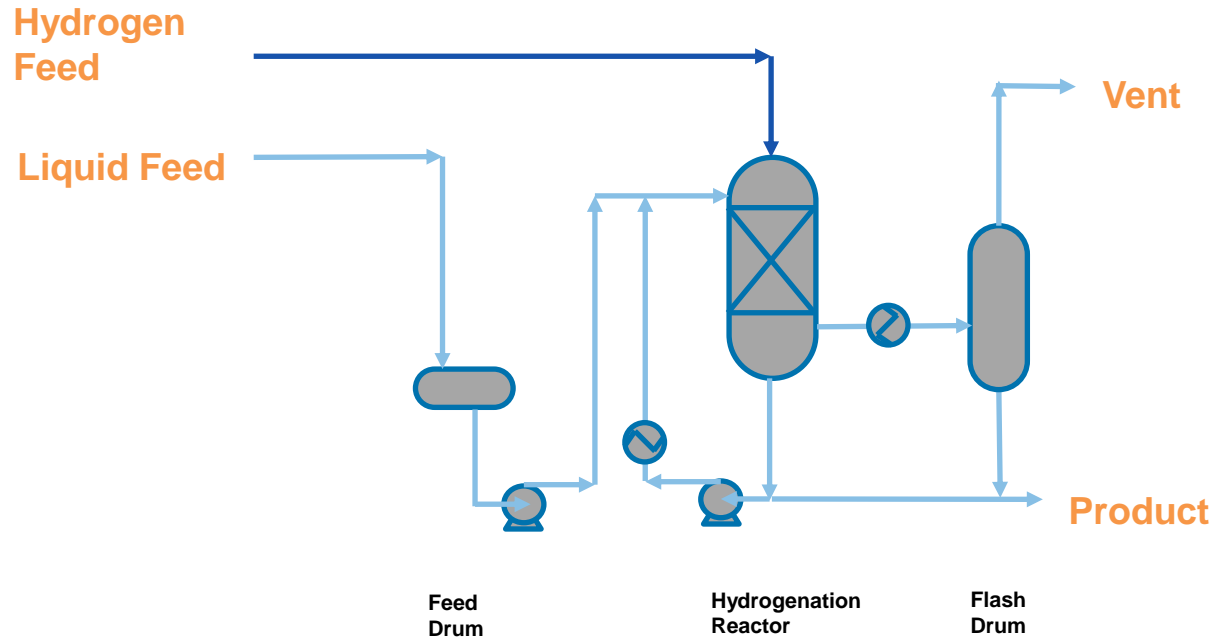
2 + 1 (a.k.a. Merry-Go-Round, two in series with one spare)



Lead-Lag with one spare



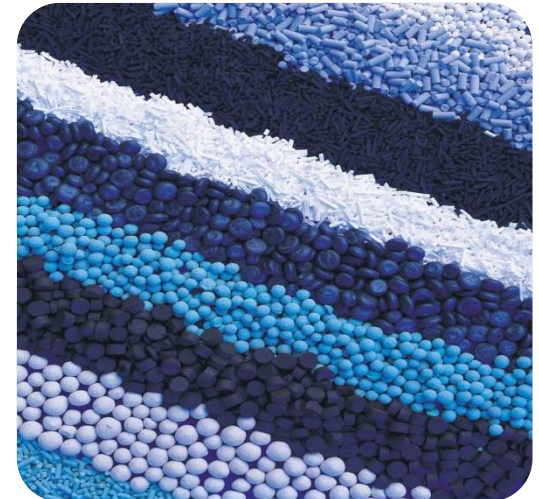
Recycle Reactor



$$\frac{r}{f} = \frac{C_f - C_i}{C_i - C_p} = \frac{C_f - C_p}{\Delta} - 1$$

3. Catalyst Selection

1. Active metal
 - i.e. hydrogenations: Pd, Pt, Ni, Cu, Co, Fe
 2. Promoter
 - Depends on the required effect: Ag, Au, Mo, W, Pb, Sn
 3. Carrier (Support)
 - Alumina, Silica, Zeolite, Carbon
 4. Shape
 - sphere, extrusion, tablet
 5. Size
 - 1 mm to 6 mm
- Standardized product by application



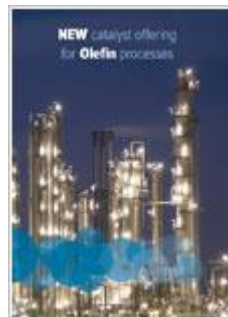
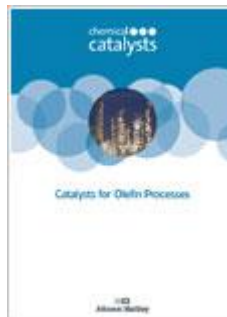
Catalyst Development

- In-house state of the art testing facilities
- Gas and liquid phase testing capabilities specifically designed for different olefin streams
- Test work uses synthetic feed blends to mimic industrial compositions



- Dedicated development team researching full and selective hydrogenation catalysts for various markets
- Proving on catalyst offerings under customer feed blends and process conditions

Catalysts for specific services



<http://www.jmprotech.com/literature-downloads>

Pyrolysis Gasoline

Market leading products to : -

- Improve induction period and colour
- Reduce gum content of gasoline blending components
- Reduce fouling in the downstream hydrodesulphurisation unit

Nickel catalysts

- sulphur and heavy metal tolerance
- preservation of aromatics

Palladium catalysts

- simple activation
- high olefin selectivity

Pyrolysis gasoline catalysts

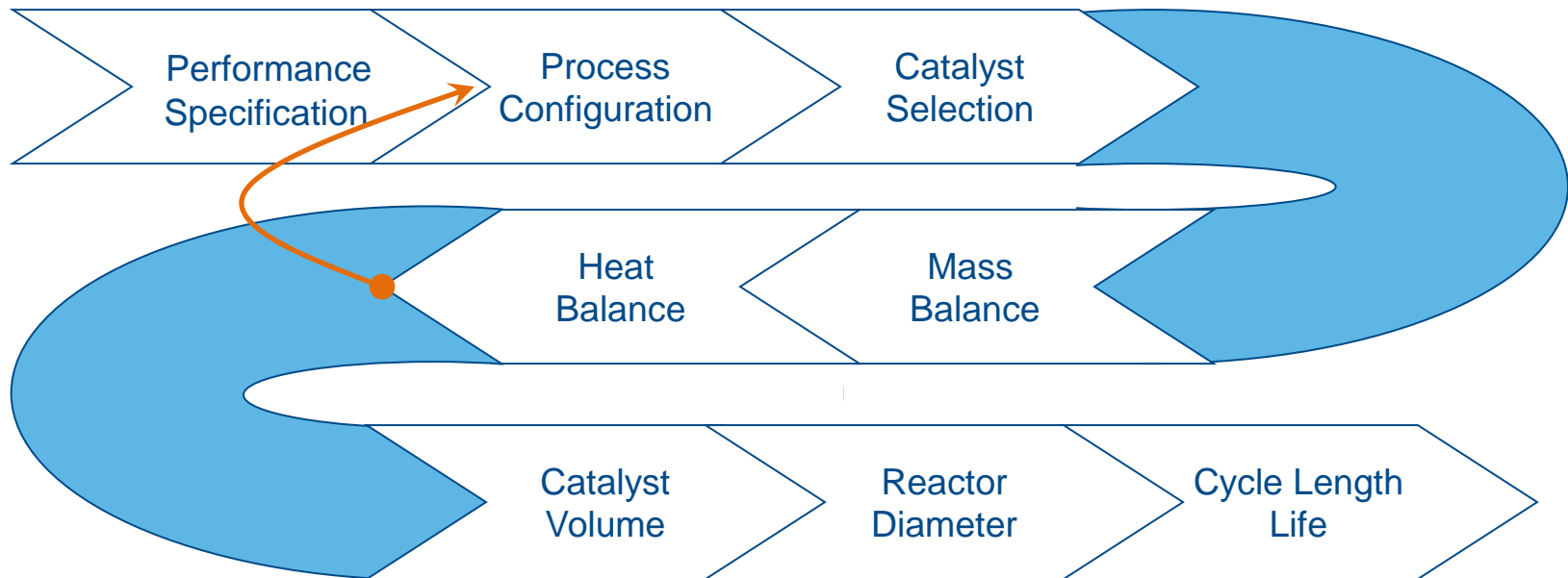
	HTC NI 200	HTC NI 400	PRICAT PD 309/6	PRICAT PD 469
Active metal	Ni	Ni	Pd	Pd
Promoted	no	no	no	no
Size (mm)	2.5	2.5	2.5	2 - 4
Shape	trilobe extrudate	trilobe extrudate	trilobe extrudate	sphere
Support	alumina	alumina	alumina	alumina

Available in four different types to suit different activation situations

Types of HTC NI catalyst

	OX	OXS	RP	RPS
Reduction temperature	high	moderate	low	lowest
Sulphur addition	standard	none	standard	none

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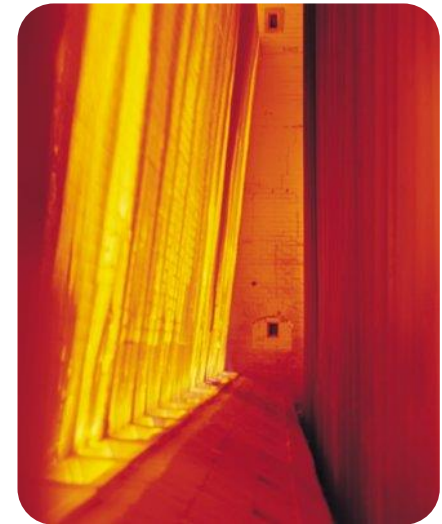
4. Material Balance

- Ch.E. 101
- Moles!
- Conversion for spec component
- Account for every reaction
- Amount of “reactant” (hydrogen, oxygen, fuel)
 - i.e. H₂:Ac, scfh per bbl
 - Excess reactant
 - % conversion
- Equilibrium limits
- Recycle composition
- Vent
- Spreadsheet
- Process simulation



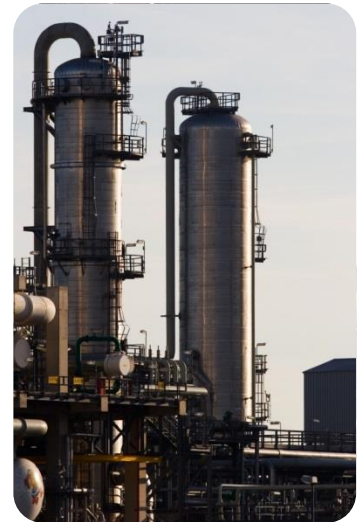
5. Heat Balance

- Required temperature
 - Minimum inlet
 - WABT
 - EIT
- Heat of Reaction
 - Heat of formation
 - Heat of combustion
- Pressure Effects
 - Dew point
 - Bubble point
 - V / L split
- VLE Data
- Spreadsheet?
- Process simulation

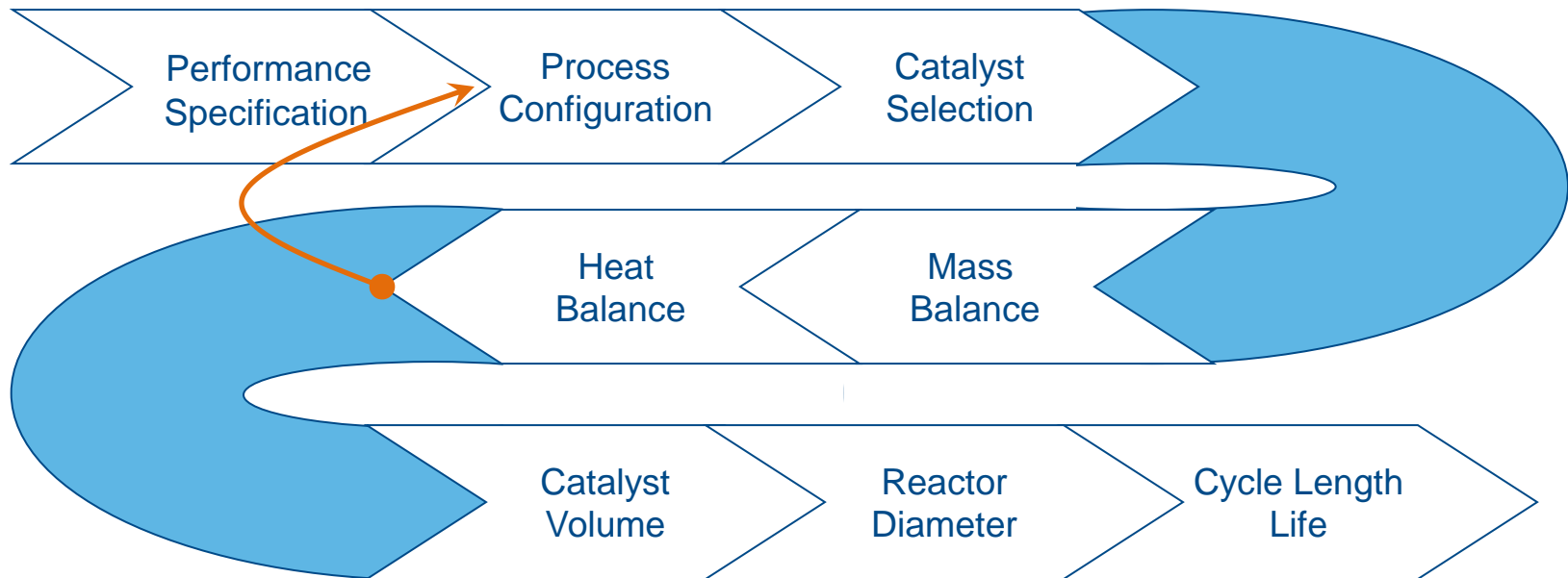


Heat and Material Balance Issues

- Poor performance if temperature rise is greater than 75°F (42°C) per bed
 - Activity & selectivity issues
 - Increase recycle
 - Add another bed in series
- Must be at least 15°C (25°F) above the dew point to prevent condensation on catalyst
 - Feed superheat
 - Intercooler operation
- Hydrogen solubility issues
 - Choose thermo package carefully
 - 2-phase feed more complicated than single phase
- Vaporization due to heat of reaction
 - Channeling
 - Hot spots



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6. Catalyst Volume - Practice

- Required contact time (τ) determined by laboratory performance testing and experience
- Kinetic theory can provide interpolation for alternate conditions.
- Rates are normally transformed for nominal conditions
 - SI = 1 atm, 0°C = Nm³/hr per m³ of catalyst
 - USCU = 14.7 psia, 60°F = scfh per ft³ of catalyst (6% higher for gas!)

$$GHSV = \text{gas hourly space velocity} = \frac{\text{Volumetric Feed rate}}{\text{Catalyst Volume}} \propto \frac{1}{\tau}$$

$$LHSV = \text{liquid hourly space velocity} = \frac{\text{Volumetric Feed Rate}}{\text{Catalyst Volume}} \propto \frac{1}{\tau} \quad \text{hr}^{-1}$$

$$WHSV = \text{weight hourly space velocity} = \frac{\text{Mass Feed Rate}}{\text{Catalyst Mass}} \propto \frac{1}{\tau}$$

7. Reactor Diameter

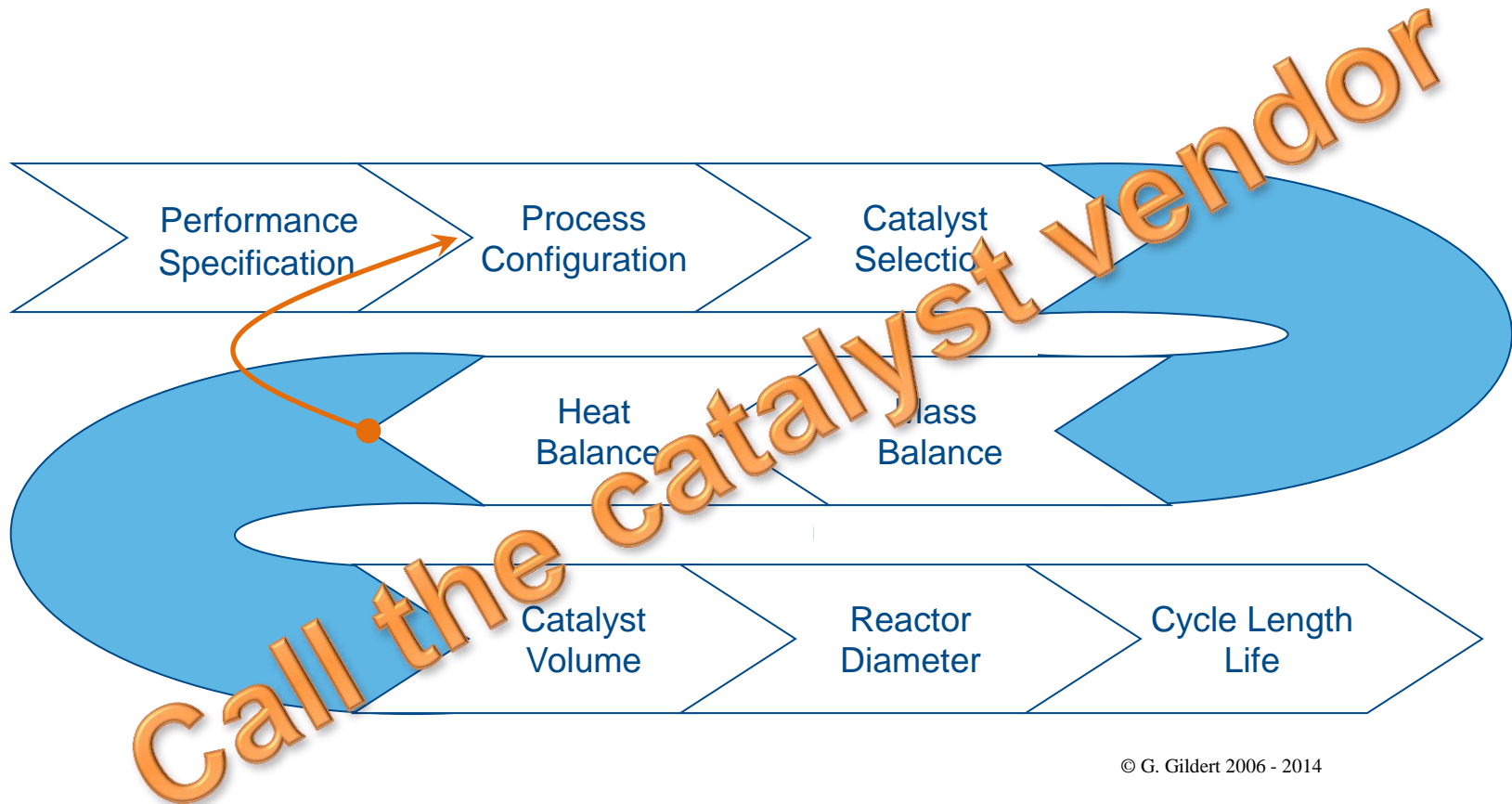
- $L/D = 1/2$ to 5
 - Radial distribution of short beds
 - Wall effects on tall beds
- Bed Height Limits
 - Maximum based on catalyst crush strength, loading, channeling
 - Minimum based on history, conversion
- Superficial Velocity
 - Maximize for mass transfer
 - Limited by channeling for 2-phase systems
 - Turbulence via Re
 - Mass Transfer via Sh
- Pressure Drop / Flow Regime
 - Process design to minimize
 - High cost & system limits
 - 2-phase flow regime for improved mass transfer = reaction rate

8. Catalyst Cycle and Life

- Cycle Length
 - Experience
 - Temperature
 - Heavies in feed
- Life
 - Number of regenerations
 - **Accumulation of poisons**
 - Average feed rate * average concentration vs. capacity



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Thank You.

Questions?

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