Johnson Matthey

The Eight Steps to Specify a Catalyst Bed

Gary Gildert
Houston, TX

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Johnson Matthey Overview

- A speciality chemicals company and a world leader in advanced materials technology
- Origins date back to 1817, floated 1942, FTSE 100 company since June 2002
- Market capitalization of approximately £4.5 billion
- £12 billion revenue and underlying profit before tax* of £426 million for year ended 31st March 2012
- Operations in over 30 countries with 10,000 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.

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Chemical Catalysts Business

Supply the catalyst and service demands of the following major global market segments

- **Olefins:** feedstock purification, full and selective hydrogenation of a variety of olefinic streams such as acetylene, pyrolysis gasoline, ethylene cracker products, benzene to cyclohexane, phenol and AMS hydrogenation
- **Alcohols**: feedstock purification, hydroformylation, process licencing, oxo-aldehyde hydrogenation, polishing
- **Solvents:** de-aromatisation and de-sulphurisation of hydrocarbons
- **Fluorochemicals:** fluorination and hydrogenation
- **Chemical Intermediates, including:**
  - **hydrogen peroxide** (anthraquinone hydrogenation),
  - **aniline** (nitrobenzene hydrogenation),
  - **amines** (amination, ammonolysis, and nitrile hydrogenation)
  - **polyamides** (cyclohexane, cyclohexanone, hydroxylamine, HMDA, caprolactam polishing)
  - **VOC removal**
- **Sponge Metal catalysts:** hydrogenation of polyols, nitriles, nitro groups, olefins
- **Edible Oils:** full and selective hydrogenation of edible oils and fats
- **Oleochemicals:** full and selective hydrogenation of fatty acids
- **Biorenewables:** conversion of platform chemicals lipids and sugars (including fermentation products) to chemicals

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Johnson Matthey

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.

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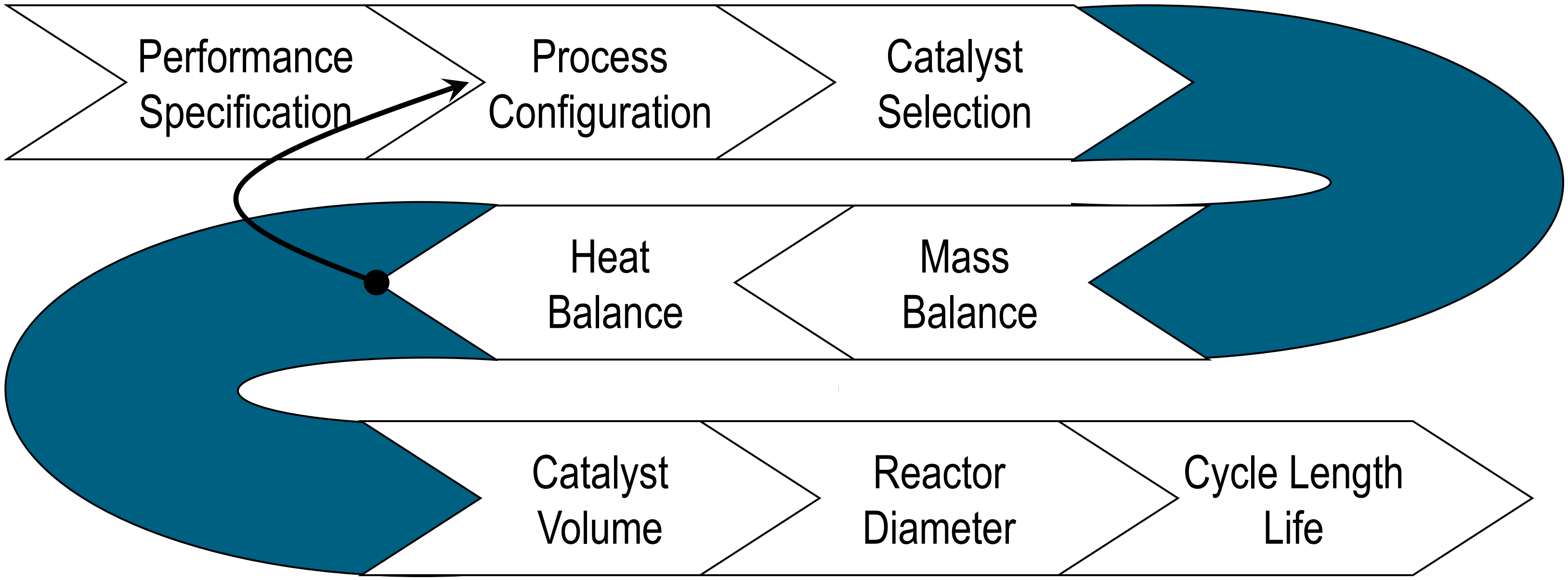
The Eight Steps



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

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Application Information

Acetylene Converter, Tail-end

Company:					Date:			
Location:					By:			
Process Information								
De-ethanizer Overheads		Normal	Maximum		**Feed Contaminants**			
Feed rate	kg/hr				H2S	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							

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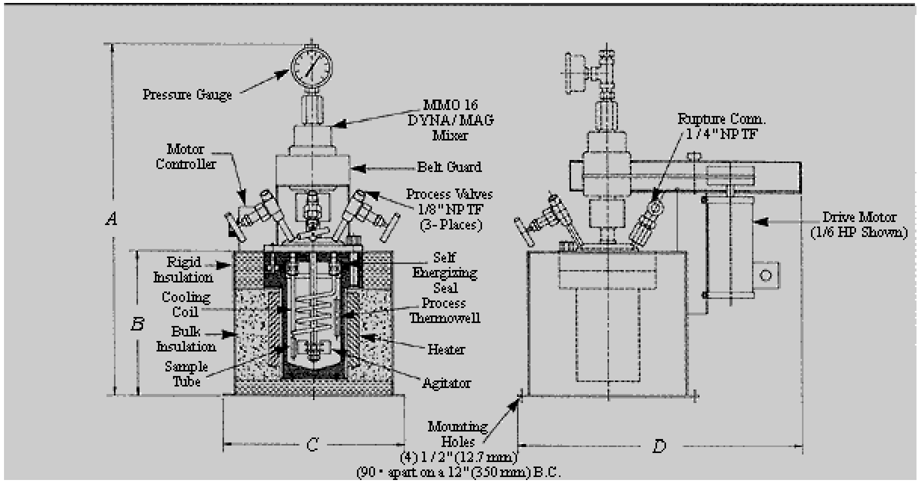
2. Process Configuration

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

2. Configuration - Batch

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



2. Batch Reactor

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

2. Configuration - CSTR

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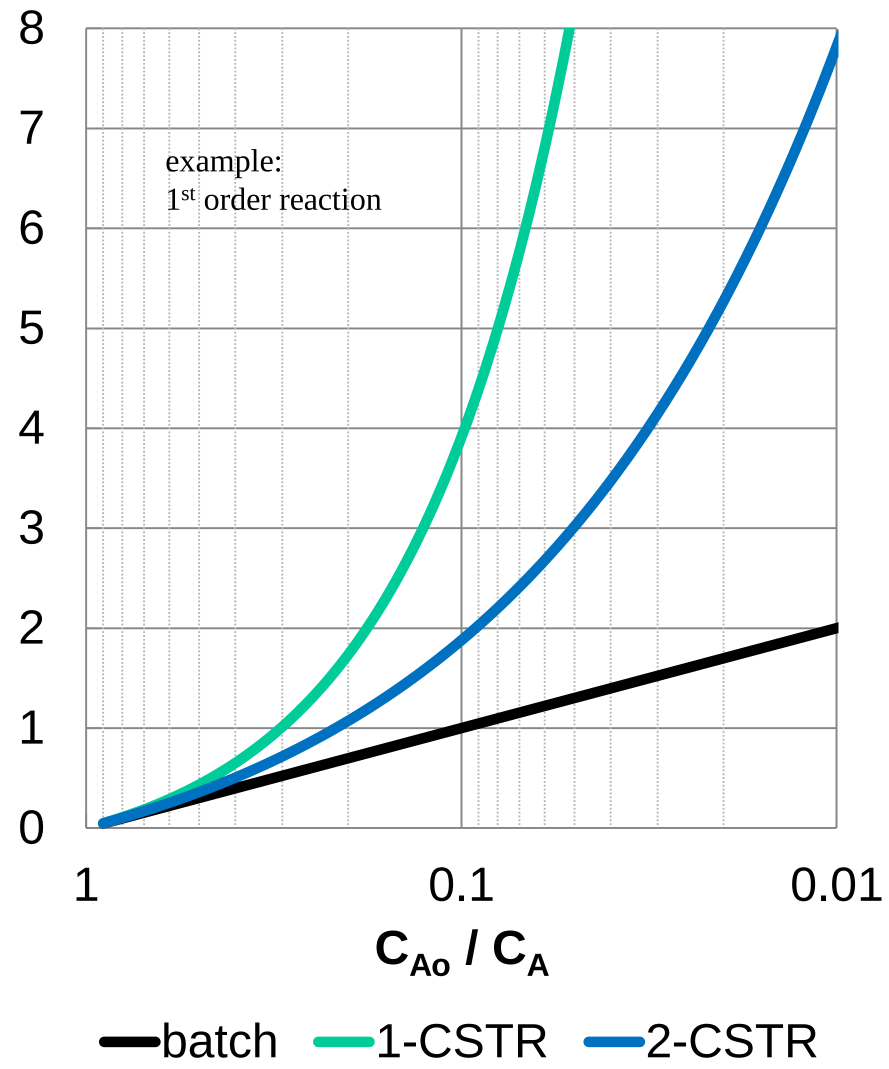
- Continuous flow
  - no fill time
  - no discharge time
  - no product heel
- Isothermal
- Low concentration
  - low fouling
  - Low reaction rate if higher order
- Higher contact time than batch?



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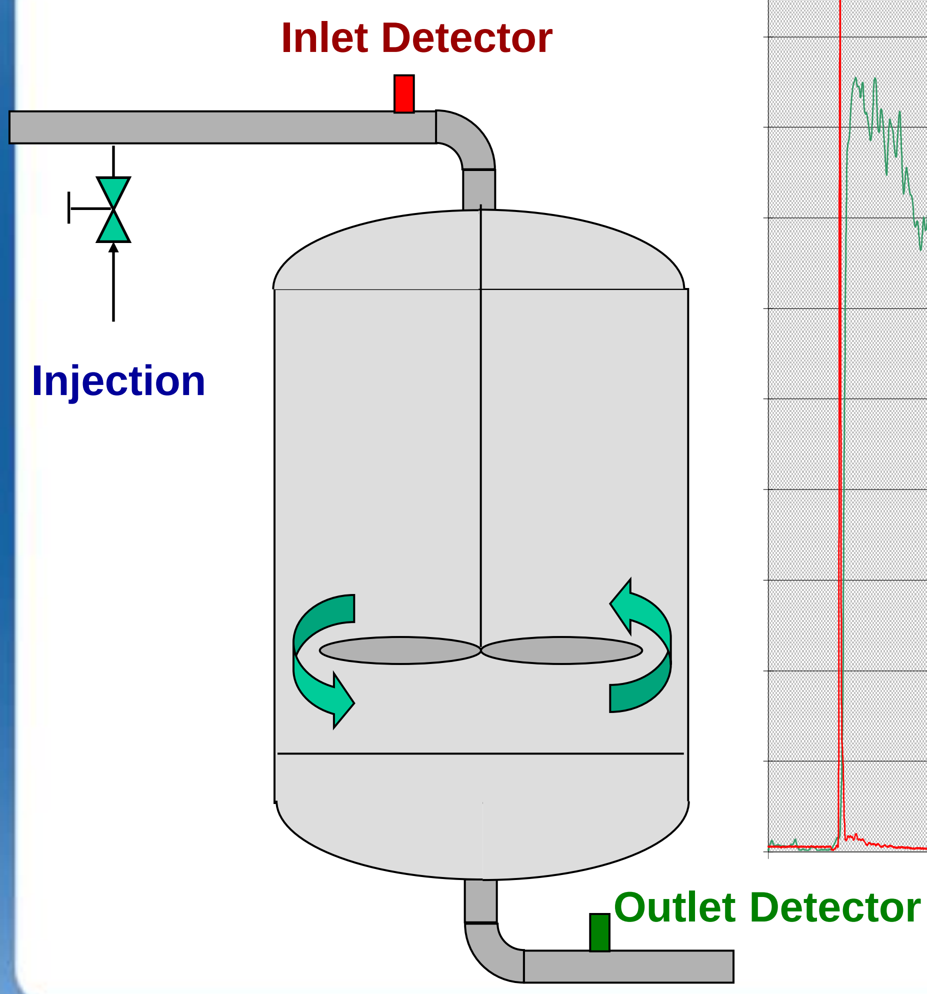
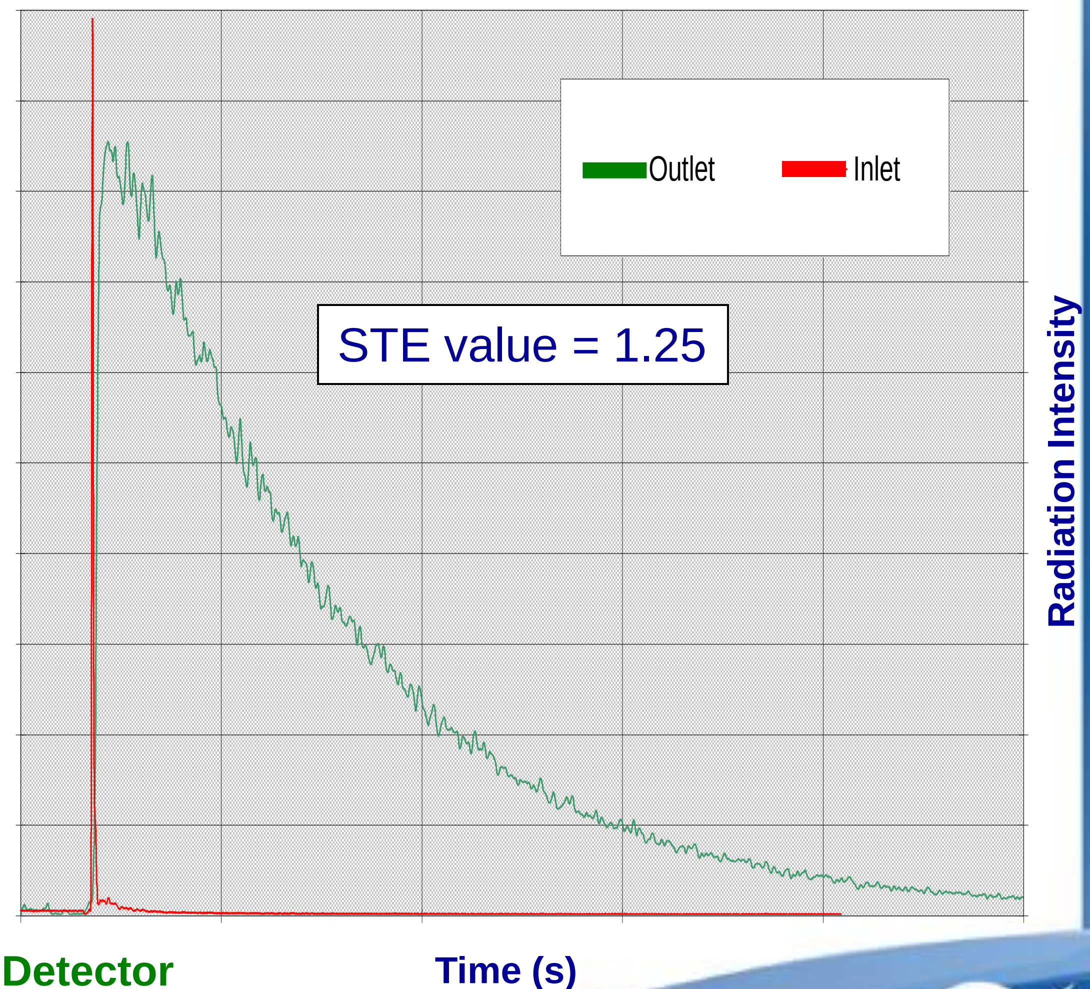
TRACERCO Diagnostics™

Residence Time of Stirred Tank Reactor





2. Configuration - PFR

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

Two Reactor Designs

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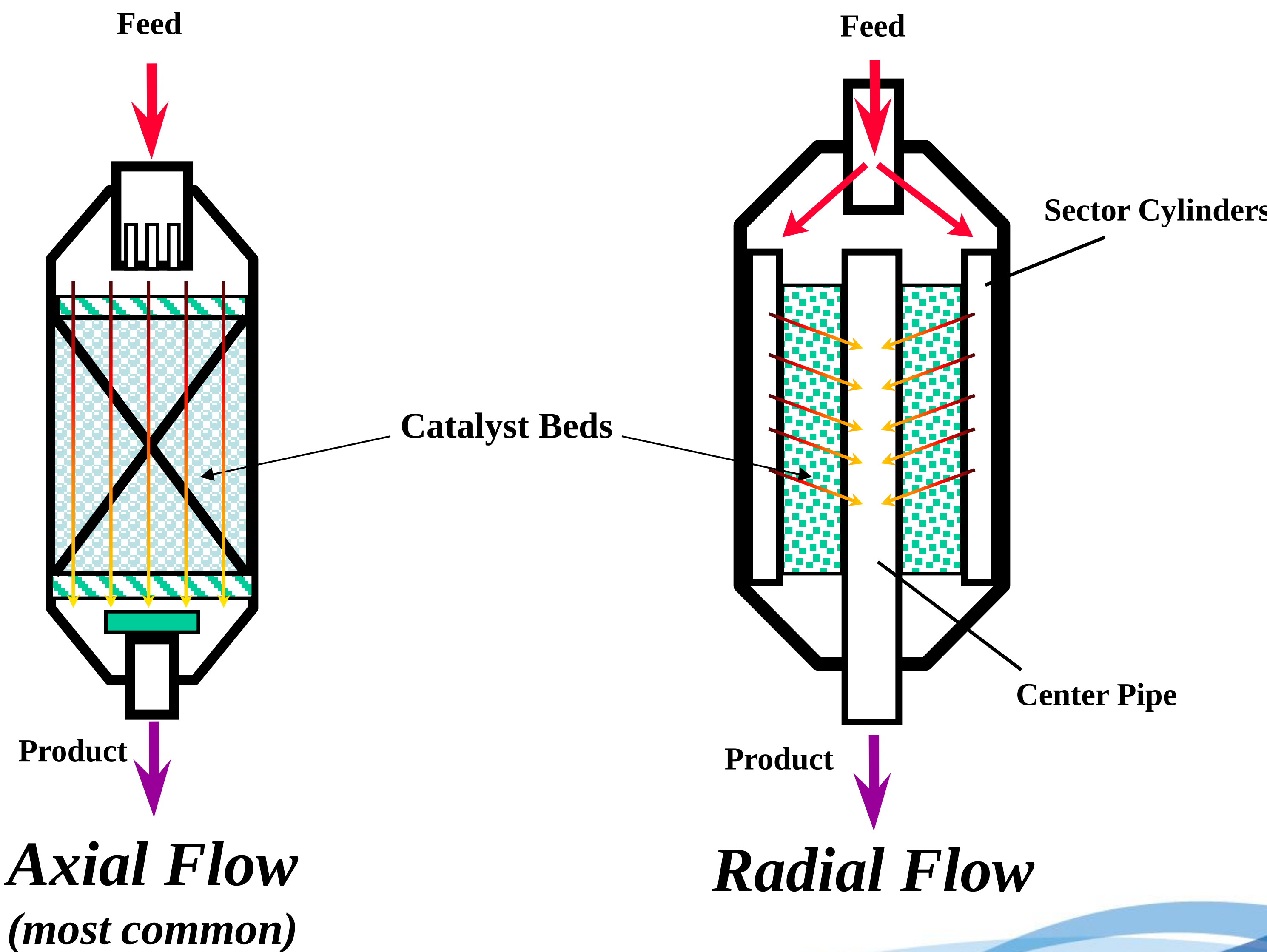
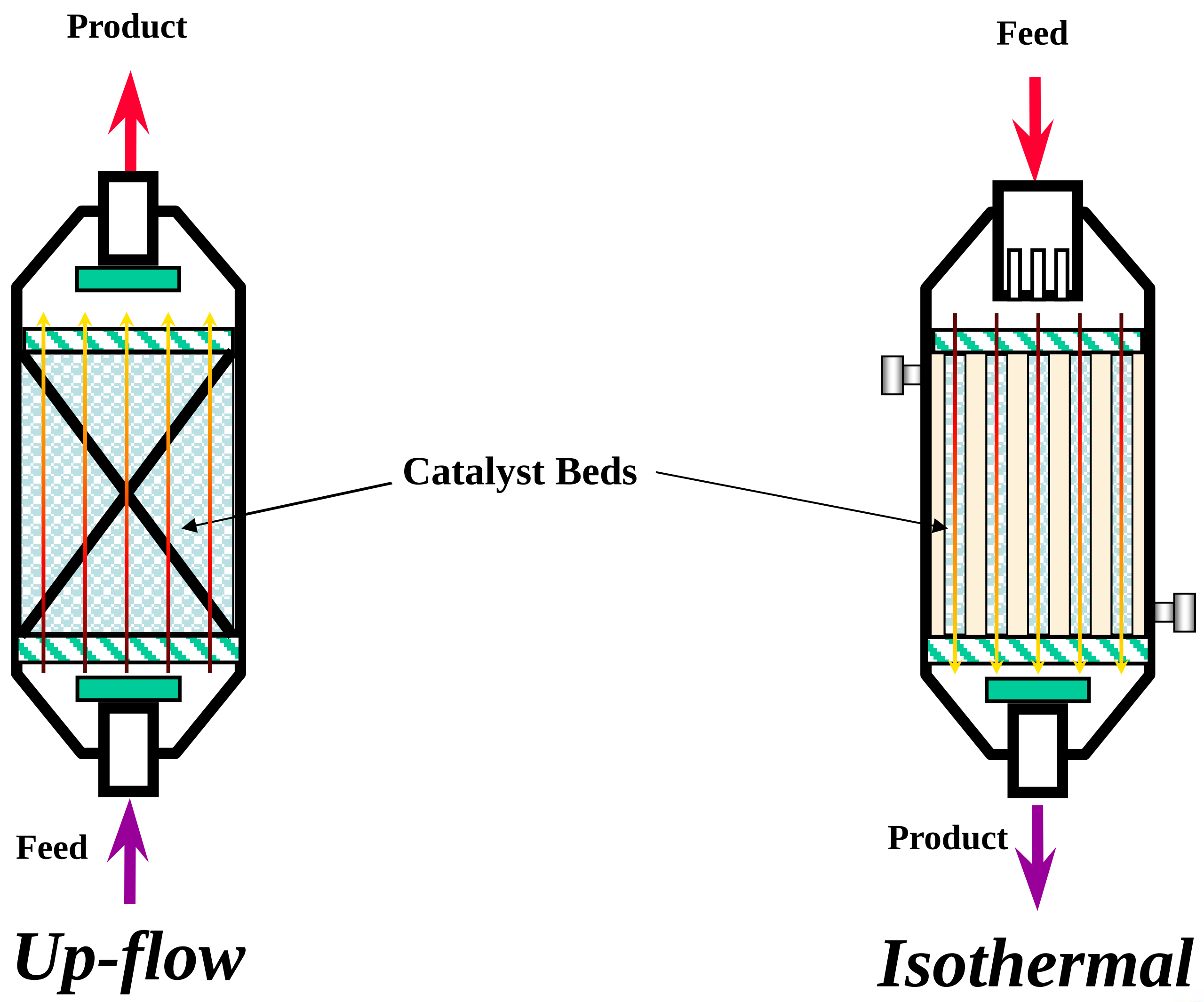
Providing Insight Onsite

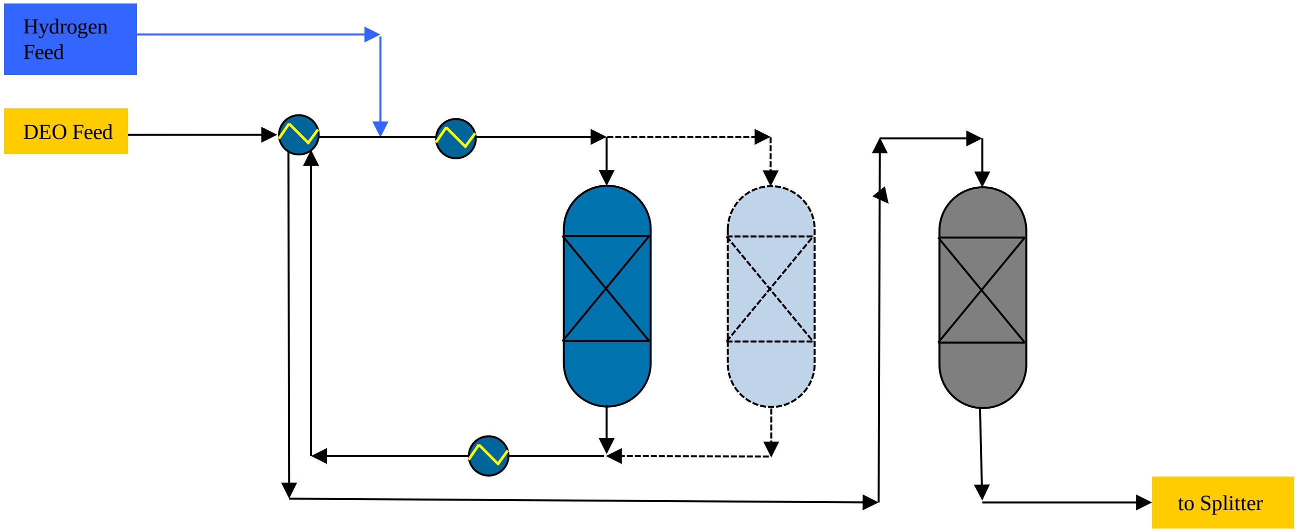


Two More Reactor Designs

Tracerco
Providing Insight Onsite



Single Bed Reactor with Spare



Feed – Effluent Exchanger | *Feed Heater* | *Effluent Cooler* | *Main Reactor* | *Spare Reactor* | *Product Dryer*

- ***Tail-end , Ethane crackers***
- ***All licensors***

2 X 2 (Two in series with two spares)

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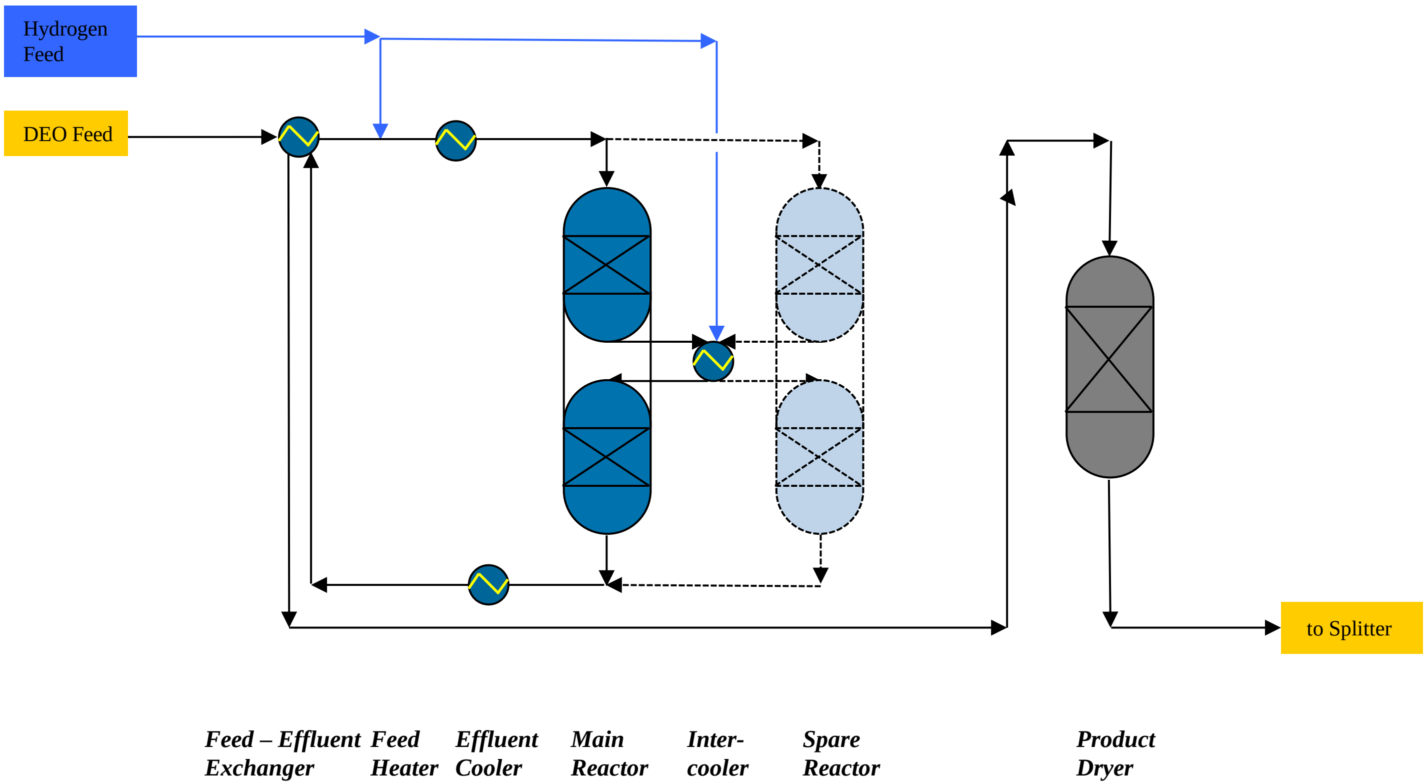

- *Tail-end , Propane and Naphtha crackers*
- *All licensors*

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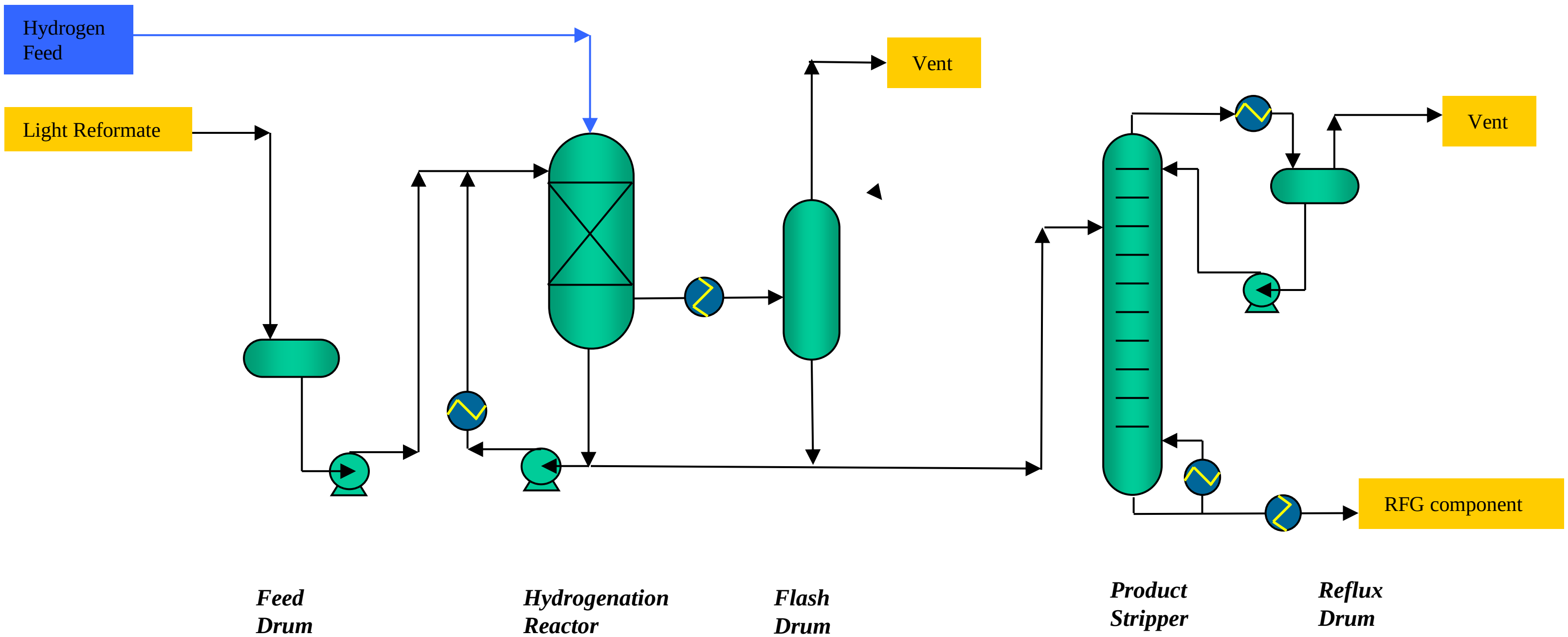
Recycle Reactor



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

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

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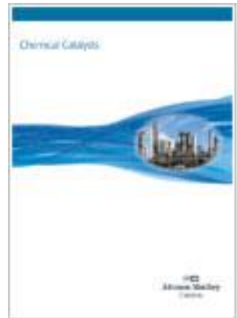
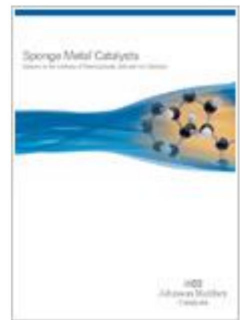
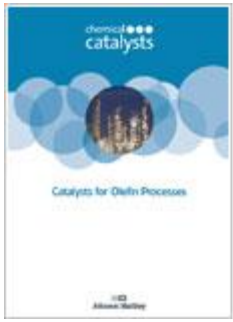
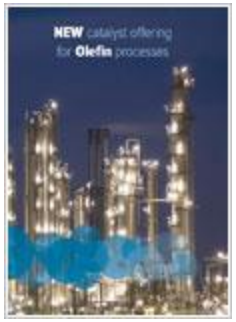
Catalysts for specific services









http://www.jmcatalysts.com/chemicalcatalysts/literature.asp

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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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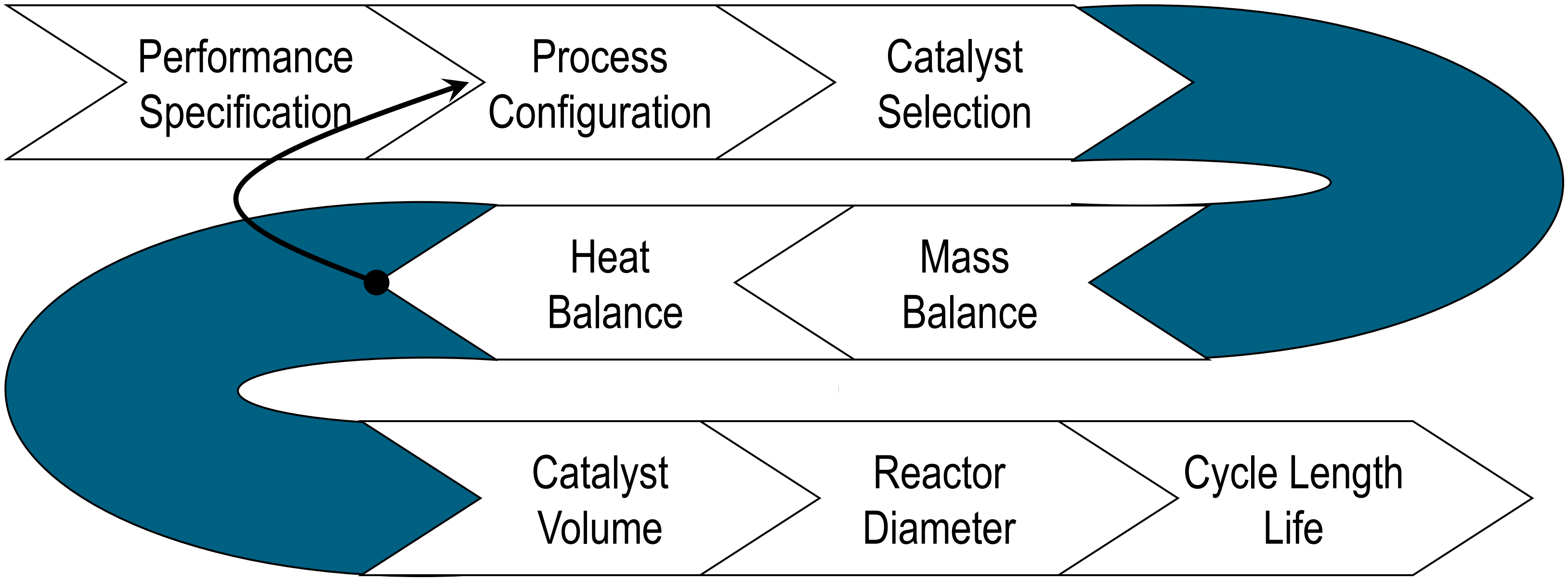

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4. Material Balance

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- 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

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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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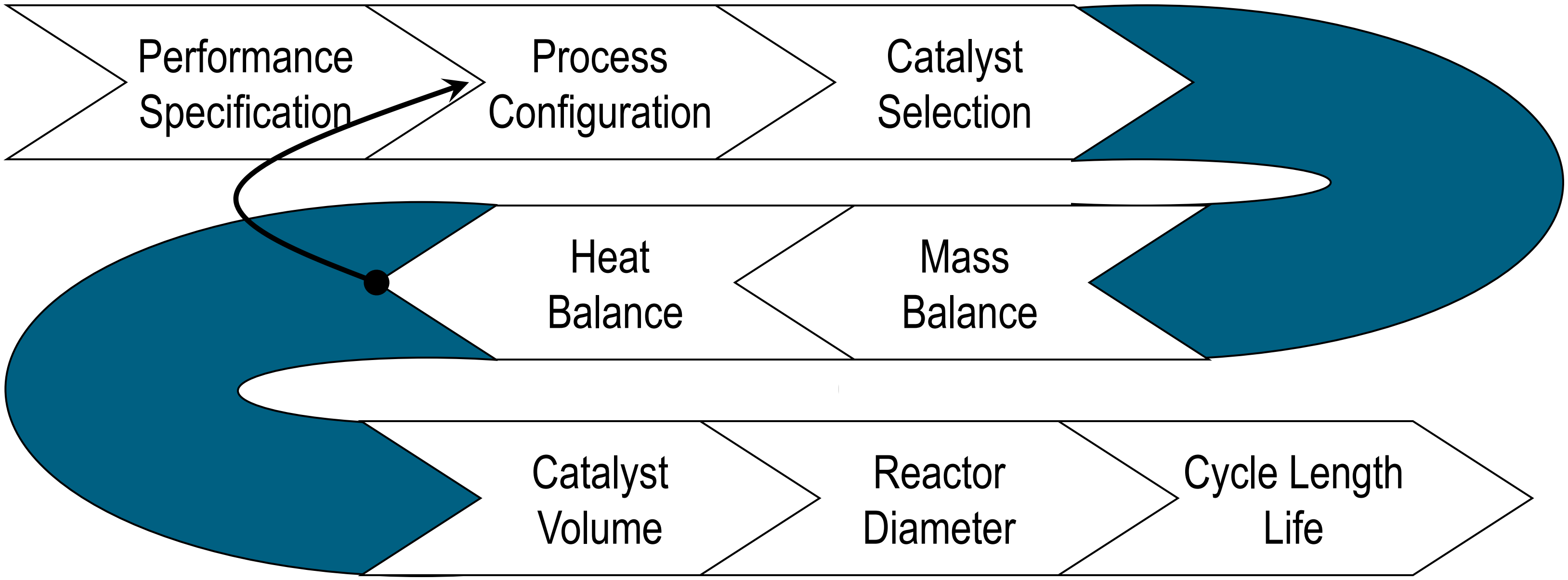

6. Catalyst Volume - Practice

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- 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 = Nm^3/hr per m^3 of catalyst
  - USCU = 14.7 psia, 60°F = scfh per ft^3 of catalyst (6% higher for gas!)

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

$$LHSV = liquid\ hourly\ space\ velocity = \frac{Volumetric\ Feed\ Rate}{Catalyst\ Volume} \propto \frac{1}{\tau}$$

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

hr^{-1}

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7. Reactor Diameter

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- L/D = ½ 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

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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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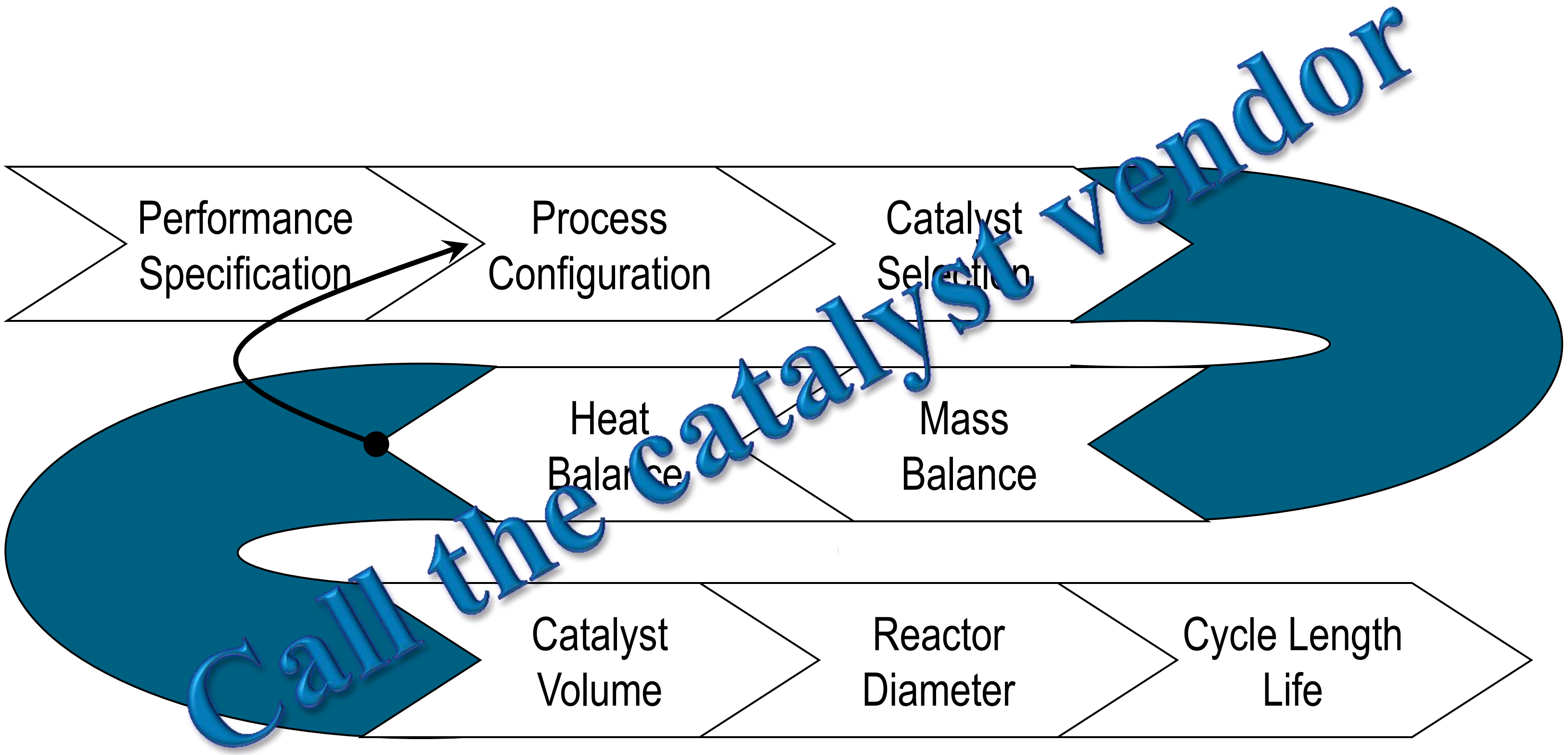

Thank You.
Questions?

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