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.
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
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

- Performance Specification
- Process Configuration
- Catalyst Selection
- Heat Balance
- Mass Balance
- Catalyst Volume
- Reactor Diameter
- Cycle Length Life

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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

**Acetylene Converter, Tail-end**

<table>
<thead>
<tr>
<th>Company:</th>
<th>Date:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location:</td>
<td>By:</td>
</tr>
</tbody>
</table>

## Process Information

<table>
<thead>
<tr>
<th>De-ethanizer Overheads</th>
<th>Normal</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed rate kg/hr</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Feed Contaminants

<table>
<thead>
<tr>
<th>Composition</th>
<th>Normal</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2S ppm m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COS ppm m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Arsine ppb w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water ppm m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Hydrogen Composition

<table>
<thead>
<tr>
<th>Hydrogen</th>
<th>Normal</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene +</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Product Specification

<table>
<thead>
<tr>
<th>Acetylene</th>
<th>Maximum</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>ppm m</td>
<td></td>
</tr>
</tbody>
</table>
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

- 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?

Example: 1st order reaction

\[
\frac{C_{A_0}}{C_A}
\]

Graph showing comparison between batch and CSTR reactors.
Residence Time of Stirred Tank Reactor

STE value = 1.25
2. Configuration - PFR

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

Axial Flow
(most common)

Radial Flow
Two More Reactor Designs

**Up-flow**

**Isothermal**

Product

Feed

Catalyst Beds

Feed

Product
Single Bed Reactor with Spare

- Tail-end, Ethane crackers
- All licensors
2 X 2 (Two in series with two spares)

- Tail-end, Propane and Naphtha crackers
- All licensors
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.jmcatalysts.com/chemicalcatalysts/literature.asp
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

<table>
<thead>
<tr>
<th></th>
<th>HTC NI 200</th>
<th>HTC NI 400</th>
<th>PRICAT PD 309/6</th>
<th>PRICAT PD 469</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active metal</td>
<td>Ni</td>
<td>Ni</td>
<td>Pd</td>
<td>Pd</td>
</tr>
<tr>
<td>Promoted</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Size (mm)</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2 - 4</td>
</tr>
<tr>
<td>Shape</td>
<td>trilobe extrudate</td>
<td>trilobe extrudate</td>
<td>trilobe extrudate</td>
<td>sphere</td>
</tr>
<tr>
<td>Support</td>
<td>alumina</td>
<td>alumina</td>
<td>alumina</td>
<td>alumina</td>
</tr>
</tbody>
</table>

Available in four different types to suit different activation situations

### Types of HTC NI catalyst

<table>
<thead>
<tr>
<th></th>
<th>OX</th>
<th>OXS</th>
<th>RP</th>
<th>RPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction temperature</td>
<td>high</td>
<td>moderate</td>
<td>low</td>
<td>lowest</td>
</tr>
<tr>
<td>Sulphur addition</td>
<td>standard</td>
<td>none</td>
<td>standard</td>
<td>none</td>
</tr>
</tbody>
</table>
The Eight Steps

Performance Specification → Process Configuration → Catalyst Selection

Heat Balance → Mass Balance

Catalyst Volume → Reactor Diameter → Cycle Length Life

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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 ($\tau$) 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!)

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

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

\[
WHSV = \text{weight hourly space velocity} = \frac{\text{Mass Feed Rate}}{\text{Catalyst Mass}} \propto \frac{1}{\tau}
\]
7. Reactor Diameter

- 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
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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Call the catalyst vendor

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Thank You. Questions?

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