bbl

Information given during last lecture:

- "It's a barrel of oil, bbl must be some silly American thing"

- bbl is an abbreviation for 1 barrel, equal to exactly 42 U.S. gallons.

- Standard Oil began manufacturing 42 gallon barrels that were blue to be used for transporting petroleum. The use of a blue barrel, abbreviated "bbl", guaranteed a buyer that this was a 42-gallon barrel.

- While North American markets typically measure oil in barrels, elsewhere oil is more commonly measured in cubic meters and less commonly in metric tonnes.

Green Chemistry

- Not a discipline
- A ‘Philosophy’
- Many facetted:
  - Chemistry
  - Engineering
  - Economics
- Sustainability

What is Green?

- Sustainable Chemistry Defined (OECD Workshop on Sustainable Chemistry, 1998)

'Within the broad framework of Sustainable Development, we should strive to maximise resource efficiency through activities such as:

- energy and non-renewable resource conservation,
- risk minimisation,
- pollution prevention,
- minimisation of waste at all stages of a product life-cycle,
- the development of products that are durable and can be re-used and recycled

Sustainable Chemistry strives to accomplish these ends through the design, manufacture and use of efficient and effective, more environmentally benign chemical products and processes.'


The 12 Principles of Green Chemistry

- A guide to a sustainable future


The 12 Principles of Green Chemistry

1. Prevention:

- Better to prevent waste than to treat or clean up waste after it has been created.
Ultra Low Sulphur Diesel

- Last few hundred ppm's are refractory high boiling sulfur compounds: mainly multi-substituted dibenzothiophenes

Combustion – Feed Ratio Dependence

Hydro-desulphurisation

HDS unit (30,000 BPD) Revamp

<table>
<thead>
<tr>
<th></th>
<th>Pre Revamp</th>
<th>Post Revamp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur, (wpmm)</td>
<td>350</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>45</td>
<td>45</td>
</tr>
<tr>
<td>Catalyst (m³)</td>
<td>46</td>
<td>180</td>
</tr>
<tr>
<td>Cycle length (years)</td>
<td>5.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Revamp of existing HDS unit for Ultra low S diesel - conventional approach-

New equipment in red

$44/T

30000 BPD

New Approach: Oxy-Desulphurization

Potential Advantages
- HDS refractory sulphur compounds are easily converted by oxidation
- ODS produces compounds easy to process downstream
- Sulfones are more polar than sulphides
- Low reaction temperature and pressure
- Expensive hydrogen is not used.

Process Specifications:
- Oxidizing agent (O2, Air, H2O2)
- Catalyst (metal oxides)
- Sulfones Separation - CO2 expanded water as solvent

Oxy-Desulphurization Approach

The 12 Principles of Green Chemistry

2. Atom Economy:
   - Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
   - Atom efficiency, E-factor

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3. Less Hazardous Chemical Synthesis:
   - Wherever practicable synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

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4. Designing Safer Chemicals:
   - Chemical products should be designed to effect their desired function while minimising their toxicity.
The 12 Principles of Green Chemistry

5. Fewer and safer Solvents and Auxiliaries:

• The use of auxiliary substances (e.g., solvents or separation agents) should be made unnecessary whenever possible and innocuous when used.

6. Design for Energy Efficiency:

• Energy requirements of chemical processes should be recognised for their environmental and economic impacts and should be minimised.

• If possible, synthetic operations should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks:

• A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives:

• Unnecessary derivatisation (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimised or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis:

• Catalytic reagents (as reactive, selective and stable as possible) are superior to stoichiometric reagents.

• “Catalysis as the main tool for green chemistry.”

10. Design for Degradation or Re-cycling:

• Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
The 12 Principles of Green Chemistry

11. Real-time Analysis for Pollution Prevention:

- Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention:

- Substances and the form of a substance used in a chemical process should be chosen to minimise the potential for chemical accidents, including releases, explosions and fires.

**EXAMPLE: Bulk vs. Fine Chemistry**

- Cost bulk chemicals: > 80% raw materials
  => process development/improvement focussed on decreasing raw material costs

  - example
    100 000 t.p.a.; raw material: $ 2/kg
    for a 1 % cost reduction
    => $ 2 mio. savings p.a.

  - Cost fine chemicals:
    - emphasis on reduction of fixed costs by process simplification

  - Example
    100 t.p.a.; fixed costs $ 40/kg;
    If the volume yield (amount produced per unit reactor volume) is doubled
    => $ 2 mio. savings p.a.
The Way Forward

To develop rationally and responsibly
CHEMICAL TECHNOLOGY FOR
GREEN CHEMISTRY
one needs to have a
MOLECULAR UNDERSTANDING
of the underlying fundamentals

Methodologies

Assessing a Reaction/Process

E-Factors

<table>
<thead>
<tr>
<th>Industry segment</th>
<th>Product tonnage</th>
<th>kg waste/kg product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refining</td>
<td>$10^6 - 10^7$</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>$10^4 - 10^5$</td>
<td>&lt; 1 - 5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^3 - 10^4$</td>
<td>5 - &gt; 20</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10^3 - 10^4$</td>
<td>25 - &gt; 100</td>
</tr>
</tbody>
</table>

*Typically represents annual production volume of a product at one site (lower end of range) or worldwide (upper end of range).

Minimise waste by greater precision
- Selectivity good judge for reaction efficiency
- Definition selectivity:
  - yield of product/amount of substrate converted

Types of selectivity:
- chemoselectivity (competition between different functional groups in a molecule)
- regioselectivity (e.g. ortho vs. para)
- stereoselectivity (enanti- & diastereoselectivity)

E-Factor

- Why does the E-factor increase going from bulk to fine chemistry?
  - stoichiometric reagents
  - multi-step syntheses

- If define process efficiency: “utilisation of key organic raw material”

=> often INCREASE in E-factor

Atom Economy

- How many ATOMS OF REACTANTS end up in the:
  - FINAL PRODUCT
  - BY-PRODUCTS/WASTE

- Percentage atom economy, calculate as:
  - 100 time the molecular mass (MM) of all atoms used to make the desired product divided by the MM of all reactants.
Definitions

Yield = Conversion x Selectivity
Selectivity = Yield/Conversion
Conversion = Yield/Selectivity

% Selectivity = 100 x Yield of desired product
% Amount of substrate converted

% Atom Economy = 100 x Relative molecular mass of desired products
Relative molecular mass of all reactants

kg (reactants + auxiliaries – product)/kg product = kg waste/kg product

E-factors and Atom Efficiency

• Atom economy (Trost):
  “Ignoring this parameter is one of the principle causes of waste in fine chemistry”

• Example: classic ethylene epoxidation
  “the calcium chloride process”

Ethylene Epoxidation

\[
\text{CH}_2=\text{CH}_2 + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CICH}_2\text{CH}_2\text{OH} + \text{HCl}
\]

\[
\text{CICH}_2\text{CH}_2\text{OH} + \text{Ca} \rightarrow \text{H}_2\text{O} + \text{CaCl}_2 + 2 \text{H}_2\text{O}
\]

\[
\text{Overall:} \quad \text{C}_8\text{H}_8 + \text{Cl}_2 + \text{Ca} \rightarrow \text{C}_9\text{H}_8\text{O}_4 + \text{CaCl}_2 + 2 \text{H}_2\text{O}
\]

\[
\text{MolWt} = 44 + 111 = 155
\]

\[
\text{ATOMIC UTILIZATION} = 44*100/155 = 28.5\%
\]

\[
\text{CH}_2=\text{CH}_2 + 3 \text{O}_2 \rightarrow \text{C}_9\text{H}_8\text{O}_4
\]

\[
\text{ATOMIC UTILIZATION} = 100\%
\]

Maleic Anhydride Production Routes

Benzene oxidation:

\[
\text{Formulas} \quad \text{weights:} \quad 78 + 4.5 \times 32 = 144 \quad 98
\]

\[
\% \text{atom economy} = \frac{100 \times 98}{78 + 144} = \frac{100 \times 98}{222} = 44.1\%
\]

Butene oxidation:

\[
\text{Formulas} \quad \text{weights:} \quad 56 + 3 \times 32 = 96 \quad 98
\]

\[
\% \text{atom economy} = \frac{100 \times 98}{56 + 96} = \frac{100 \times 98}{153} = 64.5\%
\]

Maleic Anhydride Production Routes

• Both reactions run at ca. 400 deg. C

• Both reactions use vanadium pentoxide as catalyst

• DIFFERENT SELECTIVITY:
  – Benzene ~ 65% selectivity
  – Butene ~ 55% selectivity

• Practical atom economy = Theoretical atom economy x Selectivity

  • Benzene: 65 x 44.1 = 28.7%
  • Butene: 55 x 64.5 = 35.5%
Characteristics of General Reaction Types

<table>
<thead>
<tr>
<th>Atom economic reactions</th>
<th>Atom un-economic reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerisations/Rearrangement</td>
<td>Substitution</td>
</tr>
<tr>
<td>Additions</td>
<td>Elimination</td>
</tr>
<tr>
<td>Diels-Alder</td>
<td>Wittig</td>
</tr>
<tr>
<td>Other concerted Reactions</td>
<td>Grignard</td>
</tr>
</tbody>
</table>

How Green is Green? Green-Index

- Green metrics, reaction classification:

<table>
<thead>
<tr>
<th>Process</th>
<th>Reaction category</th>
<th>Reaction name</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-factor</td>
<td>(10.81 + 21.9 + 500 + 15 - 23.6)/23.6 = 22.2</td>
<td></td>
</tr>
<tr>
<td>Atom economy = 100 x 262.29 / (108.1 + 190.65 + 101) = 65.8%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Examples of Reaction Types

• Diels-Alder reaction

\[
\begin{align*}
\text{Dienophile} & \quad \text{Diene} \\
\text{1,4 addition to 1,3-butadiene} & \quad \text{Cyclohexadiene}
\end{align*}
\]

Zeolites: Reduce Reaction Temperature

\[
\begin{align*}
\text{Diels-Alder reaction} & \quad \text{H-zeolite} \\
0 \text{ deg. C} & \quad \text{cis-1,8-Dioxonaphthalene}
\end{align*}
\]

Thermal reaction at 150 deg. C only 5 % yield!