“Green Chemistry”

Twelve Principles of Green Chemistry:

12. Minimize the potential for accidents:

- Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents:
  - explosions,
  - fires, and
  - Release of chemicals to the environment.

Twelve Principles of Green Chemistry:

12. Minimize the potential for accidents:

- Chemical accidents can disrupt the lives of many people, destroy local environment, and can have long lasting impact on the ecosystem: Some serious ones include
- Bhopal gas tragedy (1984, leak of methyl isocyanate)
- Chernobyl nuclear accident (1986)
- Gulf of Mexico oil spill. (2010)

Twelve Principles of Green Chemistry:

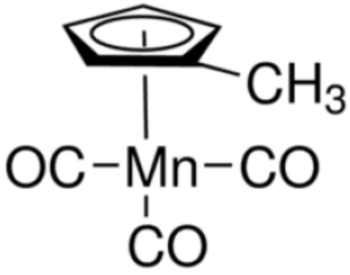
12. Minimize the potential for accidents: Some type of accidents have happened more than once!

- The Exxon Valdez case stems from the 1989 Exxon Valdez oil spill from a tanker off the coast of Alaska that dumped about 11 million gallons of oil into the water and devastated fishing communities. The U.S. Supreme Court ruled on the case in 2008 and found that Exxon had to pay punitive damages for the environmental catastrophe in the amount of $2.0 billion.

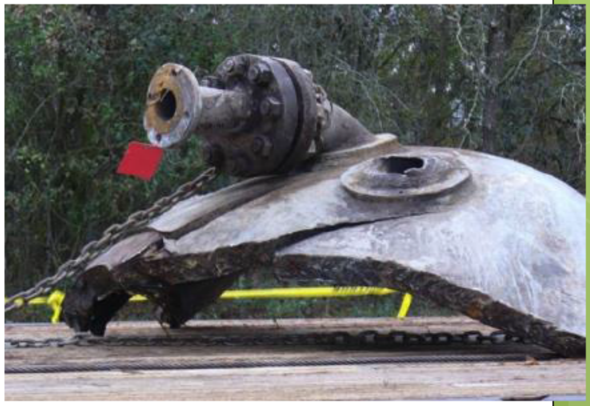
Twelve Principles of Green Chemistry:

12. Minimize the potential for accidents: Accidents can happen while running a reaction too

- A company was synthesizing a petrol additive called methylcyclopentadienyl manganese tricarbonyl (MCMT).
- The cooling in the reactor failed leading to a runaway reaction (the rate increased uncontrollably) leading to an explosion. The main reaction was only mildly exothermic but at higher temperatures, a highly exothermic side reaction started.
- The force of the explosion was such that debris ended up nearly 1.5 Km from the site.



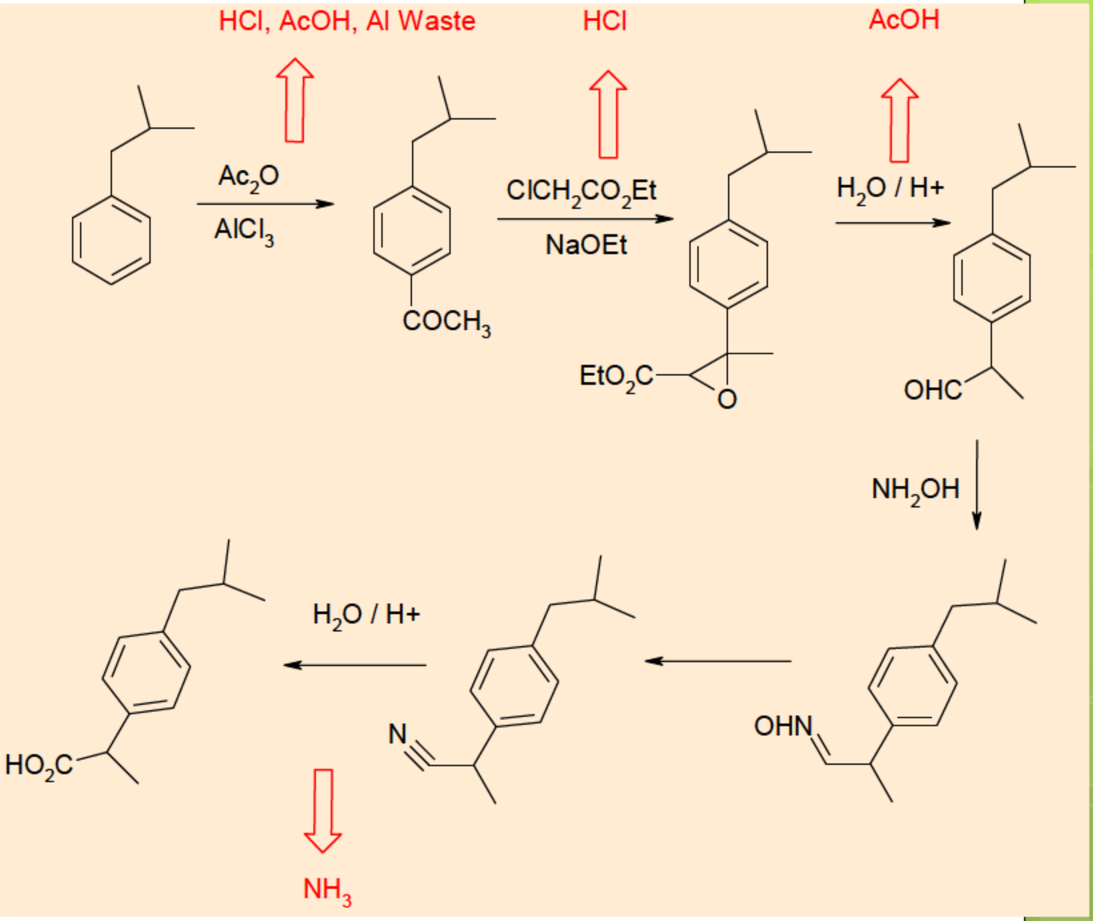
MCMT



Example of Green Chemistry Synthesis - Ibuprofen

Ibuprofen Synthesis Classic Route

- Demand:
  - 13,000 Tonnes per year (TPY)
- Developed in 1960
- 6 step reaction sequence



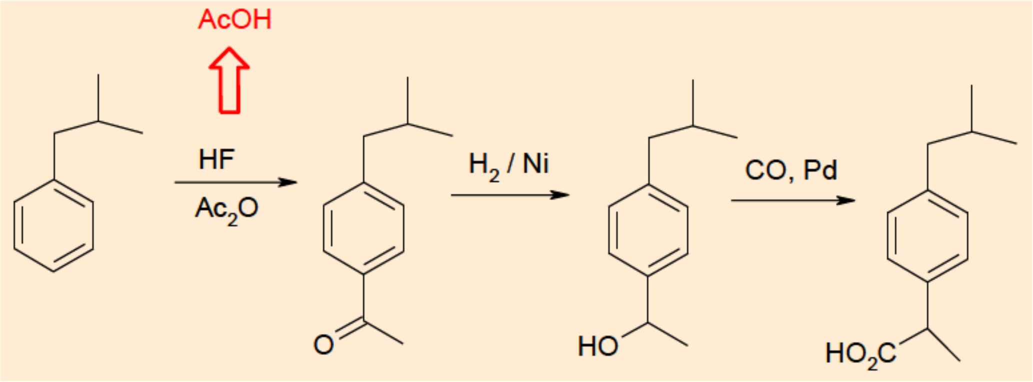
Ibuprofen Synthesis
Classic Route

- Atomic Economy: 32%
- If this synthesis were to be used today, the amount of by-products per year:

27,000 TPY

MORE WASTE THAN PRODUCT!!!

Boots & Hoechst Synthesis of Ibuprofen – Green Route



Developed to improve production:

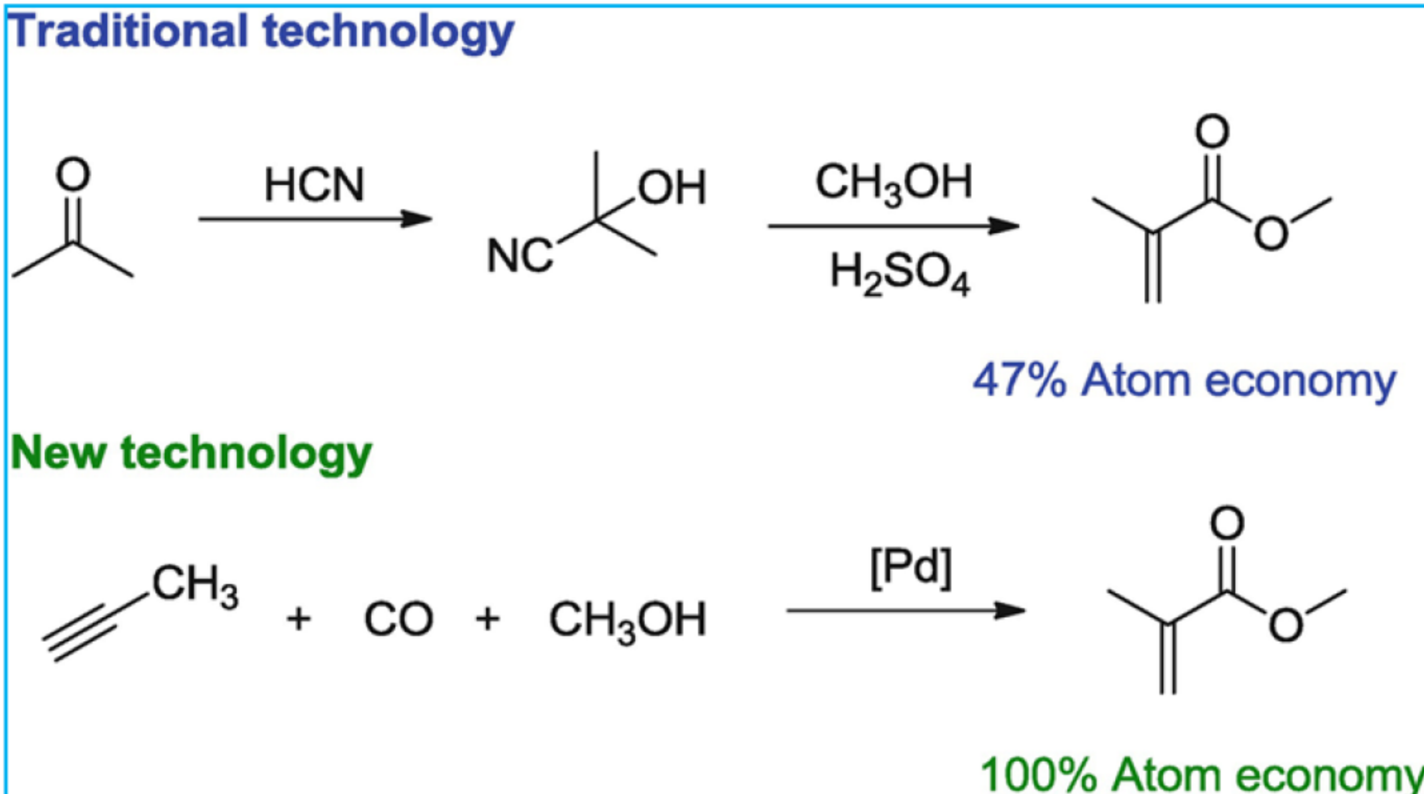
* 3 steps
* No solvents
* Catalytic vs. stoichiometric reagents
* Recycling, reuse and recovery of byproducts and reagents (**acetic acid >99%; HF >99.9%)**

Boots & Hoechst Synthesis of Ibuprofen – Green Route

- Atomic Economy 77%
- Faster
- More % yield
- Less waste produced

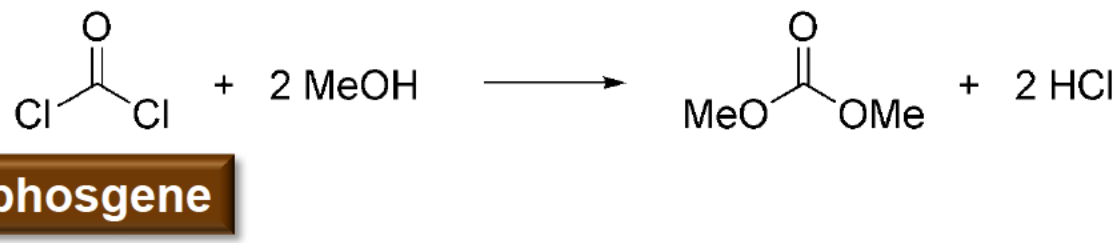
Boots an

New Chemistry can be used to render old processes more Green

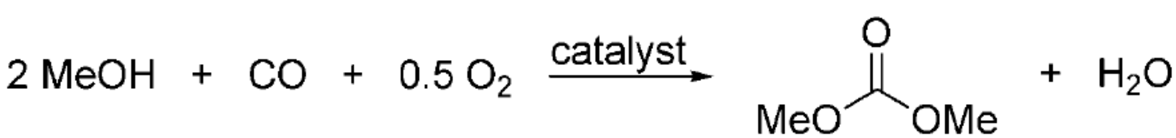


- Sometimes it is easy to compare two reactions
- Among the two syntheses of dimethyl carbonate shown below , which is greener?

1. Traditional synthesis from phosgene and methanol



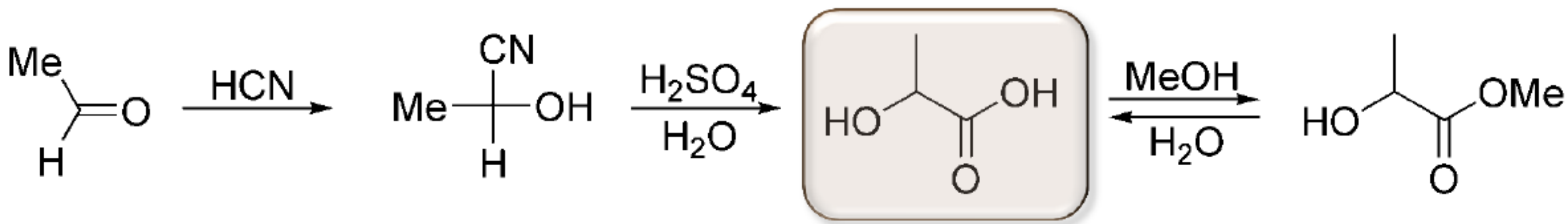
2. Modern synthesis - methanol carbonylation



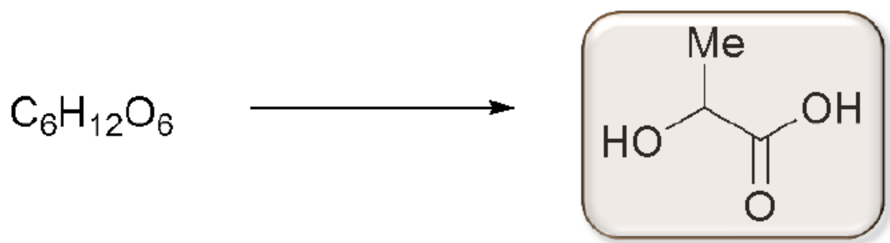
Route 2 is preferred since it avoids the use of phosgene and it gives less harmful side-products (route 2 also produces purer product, so energy intensive purification steps are eliminated).

- However, comparisons may not be straightforward in all cases
- Among the two syntheses of lactic acid ($HOCHMeCO_2H$) – which is greener?
- We will analyze over the next few slides but there may be no clear winner

1. Chemical – hydrocyanation of acetaldehyde

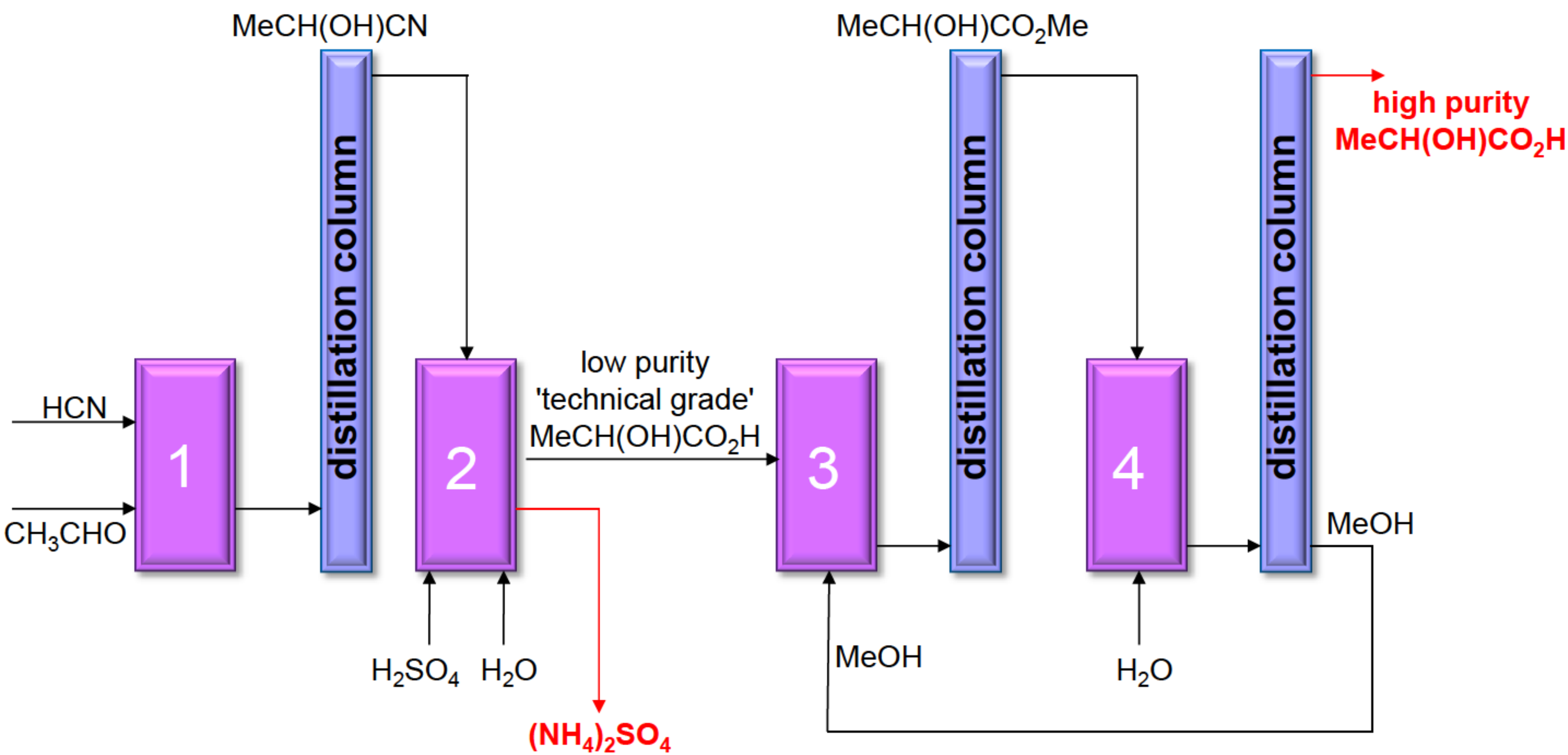


2. Biochemical – fermentation of sugars or starch



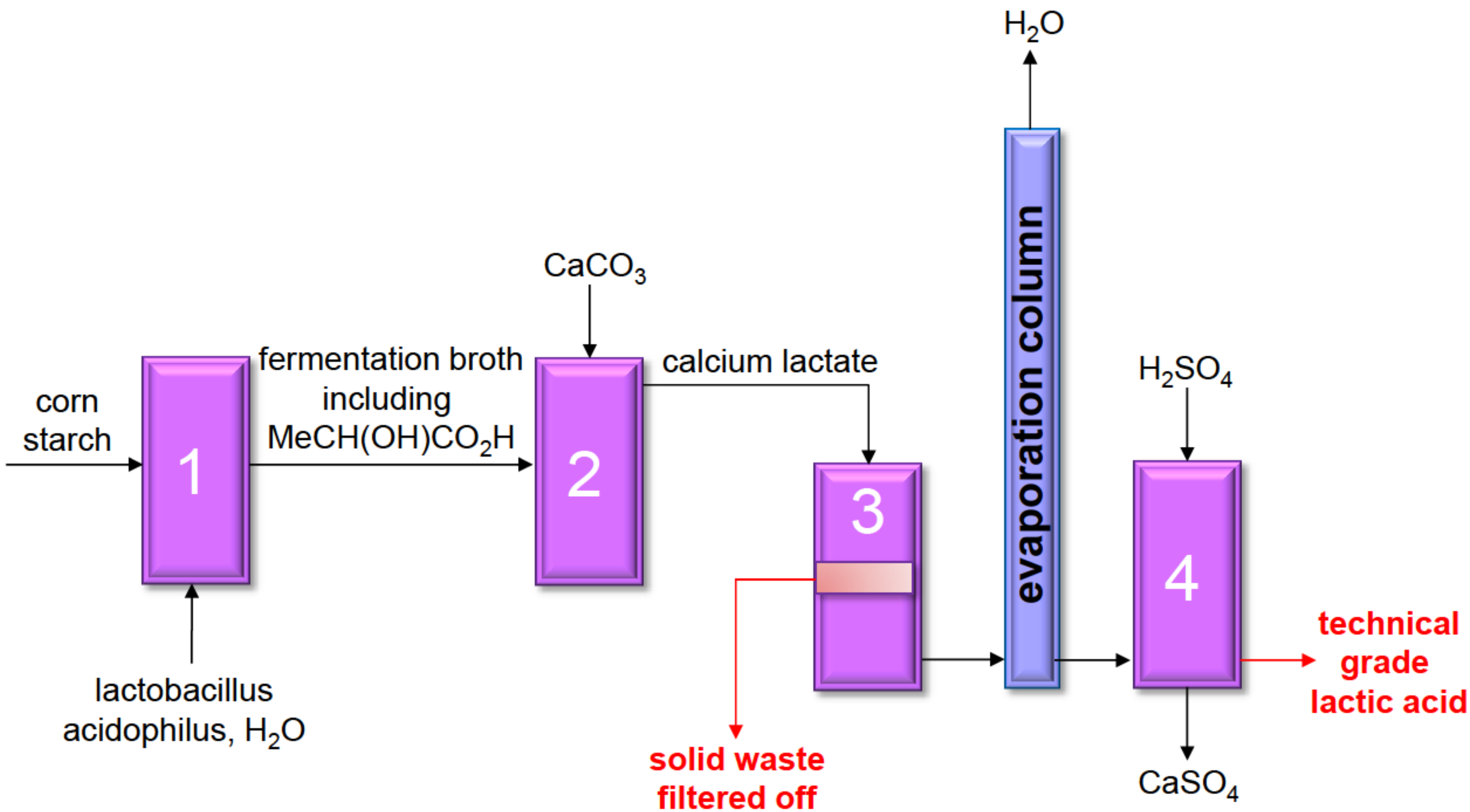
Two syntheses of lactic acid ($HOCHMeCO_2H$) - which is greener?

Chemical synthesis from CH_3CHO and HCN
Reactor 1: hydrocyanation; 2: hydrolysis; 3: esterification; 4: hydrolysis

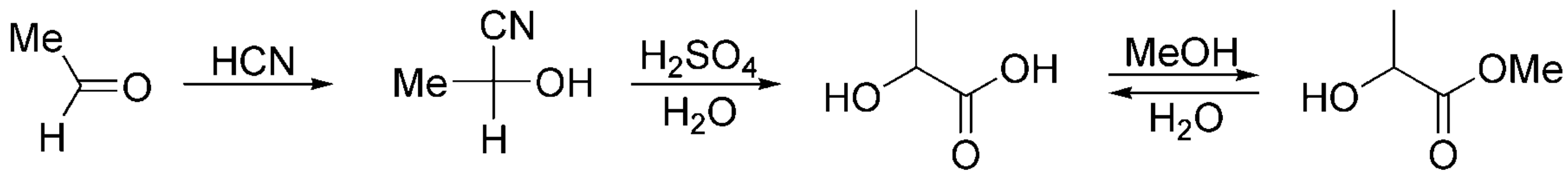


Biochemical (fermentation) route to lactic acid

Biosynthesis from starch
Reactor 1: fermentation; 2: salt formation; 3: filtration; 4: hydrolysis



Chemical synthesis of lactic acid



Advantages

- **Fast, high yielding reactions.**
- **MeOH generated in final step is recycled.**
- **Produces high purity lactic acid (> 99 %).**

Disadvantages

- **HCN is highly toxic; CH_3CHO and MeOH are also toxic.**
- **Waste stream of $(NH_4)_2SO_4$ produced (can be used as a fertiliser).**
- **Several energy intensive distillations required**

Biochemical synthesis of lactic acid

Advantages

- **Renewable feedstocks.**
- **Uses non-hazardous materials.**

Disadvantages

- **Slow (every cycle takes 4-6 days).**
- **Quantity of product per reactor volume is low.**
- **Evaporation is required (due to low salt concentration) - energetically intensive.**
- **Technical grade lactic acid (ca. 85 % purity) produced. In order to produce high purity product, the material still has to undergo the methanol transesterification process outlined on slide 10.**
- **Waste stream of $CaSO_4$ produced and very large quantities of waste water.**

Difficult to decide which is Greener….

What is green chemistry looking for?

- Waste production minimization **from the source**
- Use of catalysts
- Use of non-toxic reagents
- Use of renewable sources
- Improvement of atomic economy
- Use of non-solvent or environmental benign solvents

•The Twelve Principles of Green Chemistry: Summary

Reduction in:	1	2	3	4	5	6	7	8	9	10	11	12
Materials		■			■			■	■			
Waste	■				■				■	■		
Hazards					■						■	■
Toxicity			■	■	■					■		
Environmental impact			■				■			■		
Energy						■			■			
Cost	■	■	■		■	■		■	■			

•The Twelve Principles of Green Chemistry: At a Glance

- Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice;* Oxford University Press: New York, 1998
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  - http://www.fda.gov/Cder/OPS/PAT.htm
- EPA:
  - http://www.epa.gov/greenchemistry/index.html
- ACS Green Chemistry Institute:
  - http://acs.org
- Michael Cann, University of Scranton:
  - **http://academic.scranton.edu/faculty/CANNM1/greenchemistry.html**