
# Speciality chemicals from syngas

## IEA Task 33 workshop „Liquid Biofuels“

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# Industrial biotech press releases

| Company<br>Date of Issue | Raw Material | Fermentation<br>Volume | Product<br>Commissioning |
|---|---|---|---|
| **DSM/POET (USA)**<br>Sep 2014 | **Cellulosics from corn cobs** | **Ethanol**<br>90 kta | **Biofuel**<br>Q3.2014 |
| **Purac/BASF (D, ES)**<br>Mar 2014 | **Cellulosics** | **Succinic acid**<br>10 kt | **PBS resin**<br>Q1.2014 |
| **Evonik (DE)**<br>Jul 2013 | **Palm kernel oil** | **$\omega$-amino lauric acid**<br>**Pilot plant** | **Polyamide 12**<br>2013 |
| **Solvay/NBE (BE)**<br>Mar 2014 | **sawmill residues** | **Torrefied biomass**<br>250 kt | **Energy**<br>Q4.2014 |
| **LanzaTech (USA)**<br>Aug 2010 | **Wood residues (syngas)** | **Ethanol**<br>15 kt | **Biofuels**<br>2014 |
| **Butamax (USA)**<br>Oct 2013 | **Corn mash** | **Butanol**<br>~180 kt | **Biofuels**<br>2015 |
| **Gevo (USA)**<br>Sep 2014 | **Corn mash** | **Isobutanol**<br>28kt | **Biofuels**<br>Q4 2014 |

# Biobased Polyamide 12 (PA12)

Evonik is a leading manufacturer of PA12

- New process using Palm kernel oil as raw material
- Fewer production steps compared to chemical route
- Key step utilizes an *E. coli* strain in a fermenter
- Two phase fermentation. Pilot plant started up in 2013


Further results from the pilot plant will be the basis of the selection of the process for the next capacity expansion of PA12

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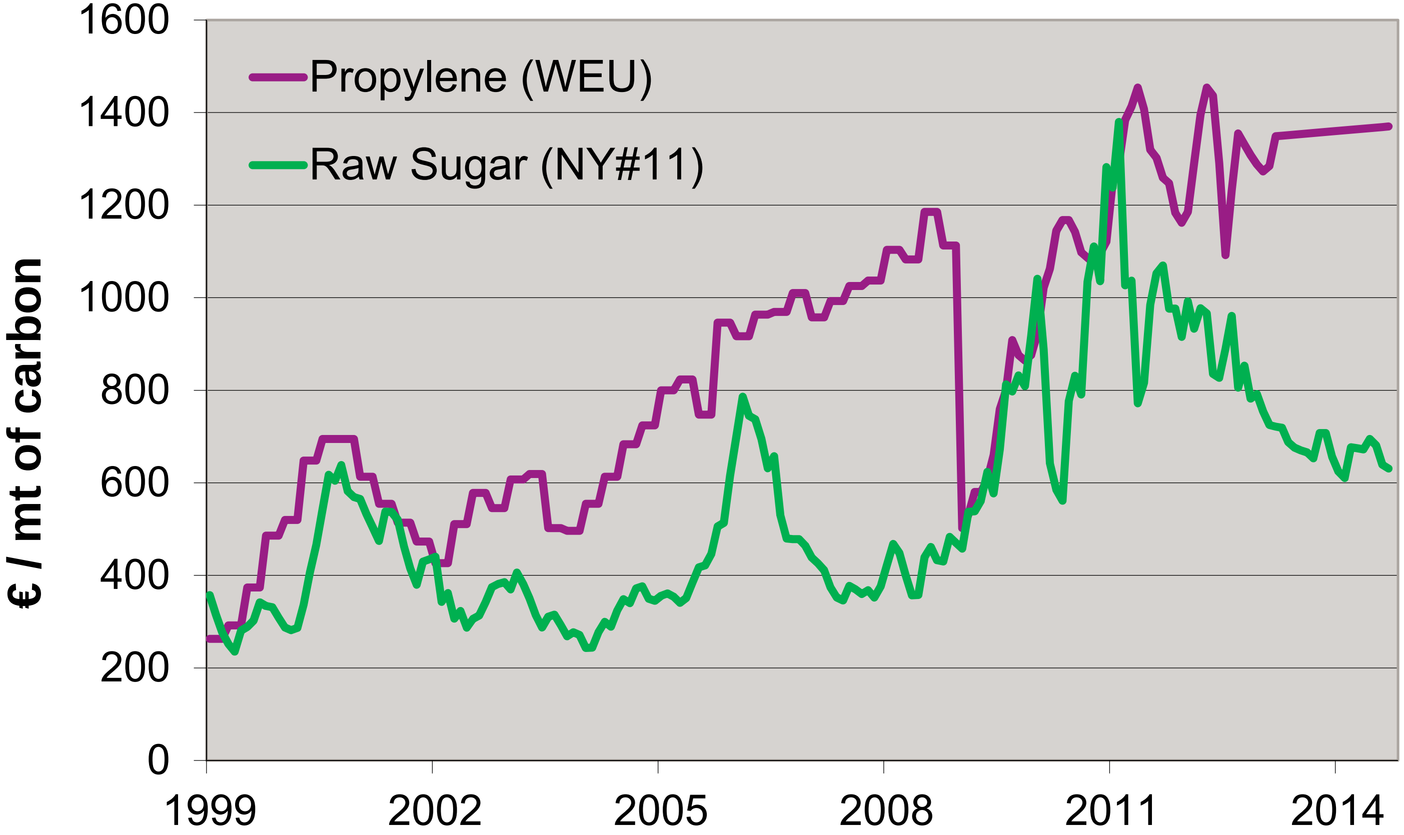
# Feedstock prices as of September 2014

| | | Production mt/a | Price €/mt | C % | O % | **Carbon €/mt** |
|---|---|---|---|---|---|---|
| **Petrochemicals** | | | | | | |
| Ethylene | $C_2H_4$ | 123 mln | 1150 | 85,6 | 0,0 | **1.343** |
| Propylene | $C_3H_6$ | 85 mln | 1105 | 85,6 | 0,0 | **1.291** |
| n-Butane | $C_4H_8$ | 12 mln | 572 | 86,0 | 0,0 | **665** |
| Crude Oil | $C_nH_{2n+1}$ | 4.000 mln | 560 | 85,0 | 0,0 | **659** |
| Natural Gas | $CH_4$ | 2.500 mln | 169 | 74,9 | 0,0 | **225** |
| **BioRenewables** | | | | | | |
| Raw Sugar | $C_{12}H_{22}O_{11}$ | 184 mln | 266 | 42,1 | 51,4 | **631** |
| Bio-ethanol | $C_2H_5OH$ | 67 mln | 508 | 52,1 | 34,7 | **974** |
| Crude Glycerol | $C_3H_8O_3$ | 2,0 mln | 233 | 31,3 | 41,7 | **743** |
| Palmkernel Oil | $C_{12}/C_{14}$ | 6,2 mln | 706 | 72,9 | 14,9 | **969** |
| Crude Palm Oil | $C_{16}/C_{18}$ | 56 mln | 565 | 75,7 | 11,9 | **746** |

**Prices** as of Sep 1, 2014, 1 € = 1.313 US$. **Volumes:** **Nexant, RAG** (petrochemicals); **F.O. Licht** (sugar, EtOH); **ICIS** (crude glycerol); **ISTA Mielke** (PKO); producer´s price (carbon dioxide) **Sources:** **Natural Gas** NAM contract (CMAI); **Propylene** EU contr. (CMAI); **Naphtha** W-EU spot (CMAI); **Raw Sugar** NYBOT#11 (ICE); **Bio-Ethanol** Hydrous, Brazil (CEPEA); **PKO** cif R´dam (Handelsblatt); **Crude Glycerol** 80%, veg. cif NWE (ICIS)

# Sugar is at least as volatile as propylene

**Price histories of propylene vs. raw sugar (carbon content)**

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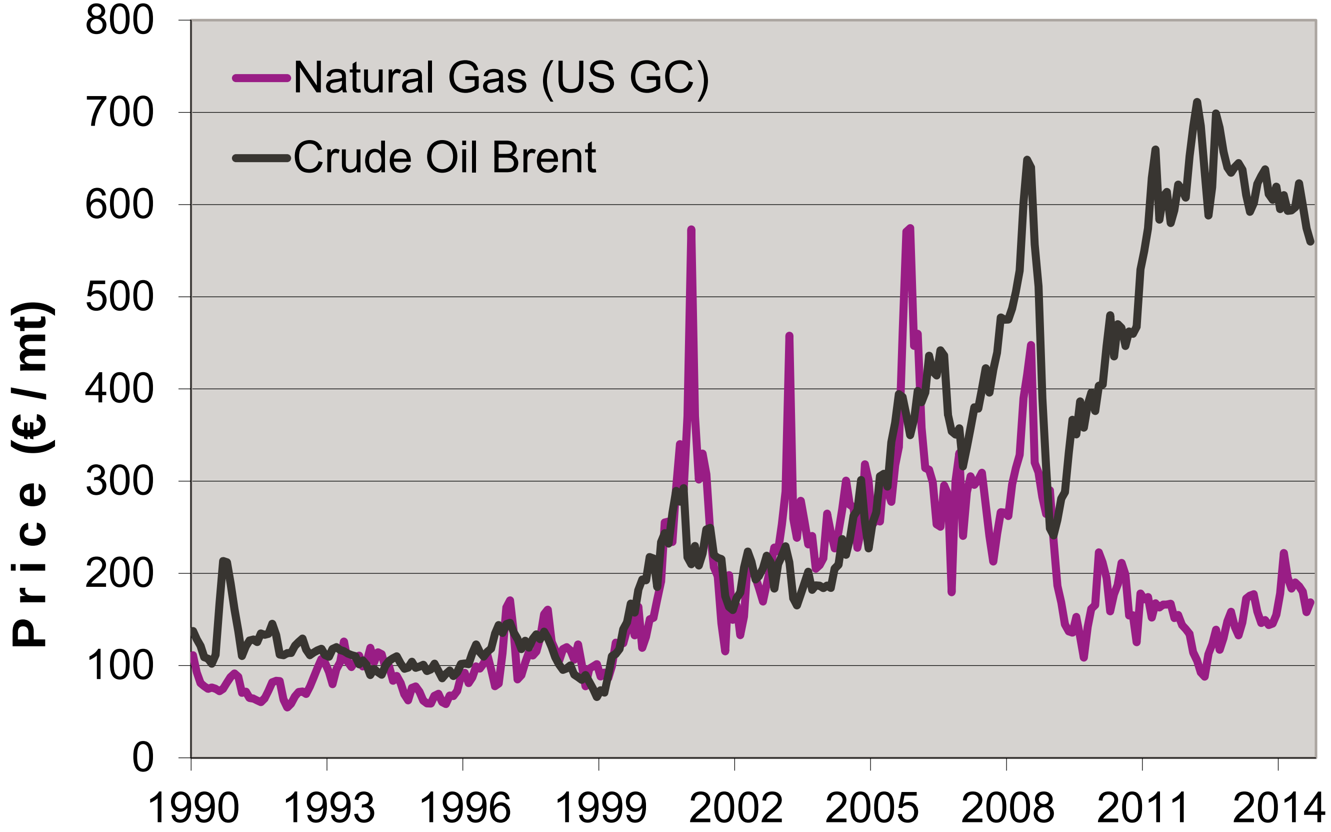
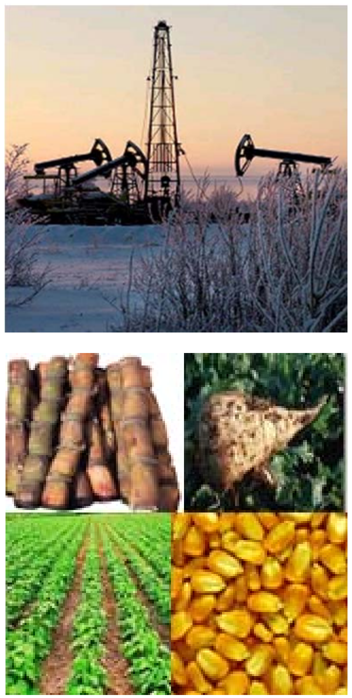
**Sources: Propylene** contract W-Europe – CMAI; **Sucrose** NY# 11 – ICE.

# The U.S. gas price has decoupled from the crude oil price

**Price histories of natural gas vs. crude oil**



**Gas has to be considered an alternative raw material**

Source: CMAI

# Syngas fermentation is 3rd generation biotechnology

| Generation | Raw material | Biotechnology |
| --- | --- | --- |
| 1st gen | Plant oils<br>Wheat<br>Corn<br>Sugar | Direct fermentation |
| 2nd gen | Biomass residues from agriculture and forestry | Lignocellulose hydrolysis<br>Integrated fermentation |
| 3rd gen | Municipal waste<br>Plant residues<br>Industrial waste gases | Syngas fermentation |

# Syngas ($CO, CO_2, H_2$) is broadly and easily accessible

**Waste streams of coke oven or steel mills**, e.g. converter gas:

$CO$, $CO_2$, $H_2$ in NRW > 2 mil. to/a

Steam reforming or catalytic oxidation of **$CH_4$ (Natural Gas)**:

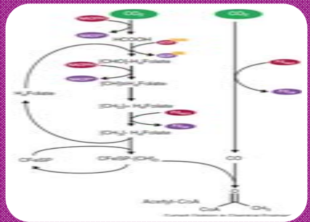
$CH_4 + H_2O \rightarrow CO + 3H_2$ $2CH_4 + O_2 \rightarrow 2CO + 4H_2$

**Biomass** gasification:

$C_6H_{12}O_6 \rightarrow 6CO + 6H_2$

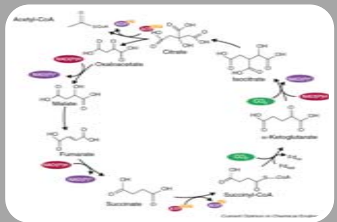
Mixing of **$CO_2$ waste streams** (e.g. power plant off-gas) with exogenic $H_2$ (e.g. from solar energy)

# Pathways utilising $H_2$ / $CO_2$ / CO



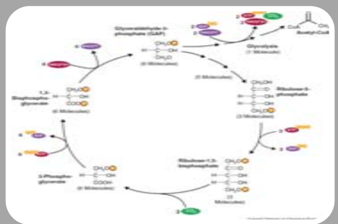
## Wood-Ljungdahl Pathway

- 100% of $H_2$-yield (theoretic)
- Clostridia (e.g. *C. ljungdahlii, C. carboxidivorans*)



## Reverse Tricarboxylic Acid Cycle

- 83% of $H_2$-yield (proven by experiments)
- *Hydrogenobacter thermophilus*

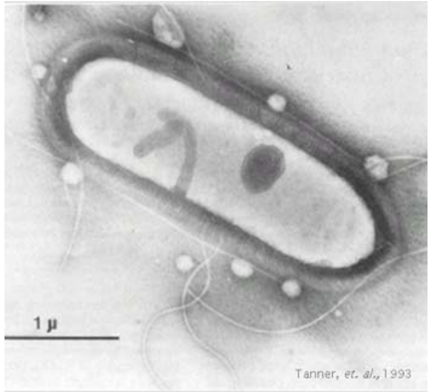


## Reverse Pentose Phosphat Pathway

- 62% of $H_2$-yield (proven by experiments)
- *Cupriavidus necator*

# Syngas digesting microorganisms synthesing chemicals of interest

**Homoacetogenic Bacteria** (*Clostridium ljungdahlii, C. carboxidivorans*)



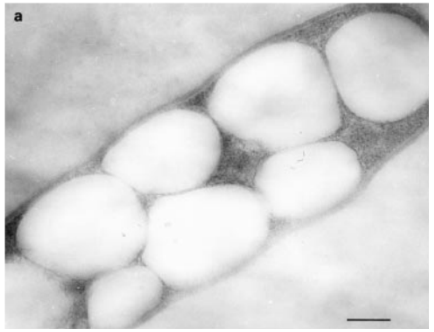

**Advantage:**

- Acetate/EtOH-Processes already established (Lanzatech et al.)
- Wood-Ljungdahl Pathway, 100% of $H_2$-yield (theoretic)

**Disadvantage:**

- Difficult to delete by-product producing pathways
- Thermodynamic limitations in the cell (acetate as by-product?)
- So far only low value products shown

**Hydrogen-Oxidizing Bacteria** (e.g. *Cupriavidus necator*)




**Advantage:**

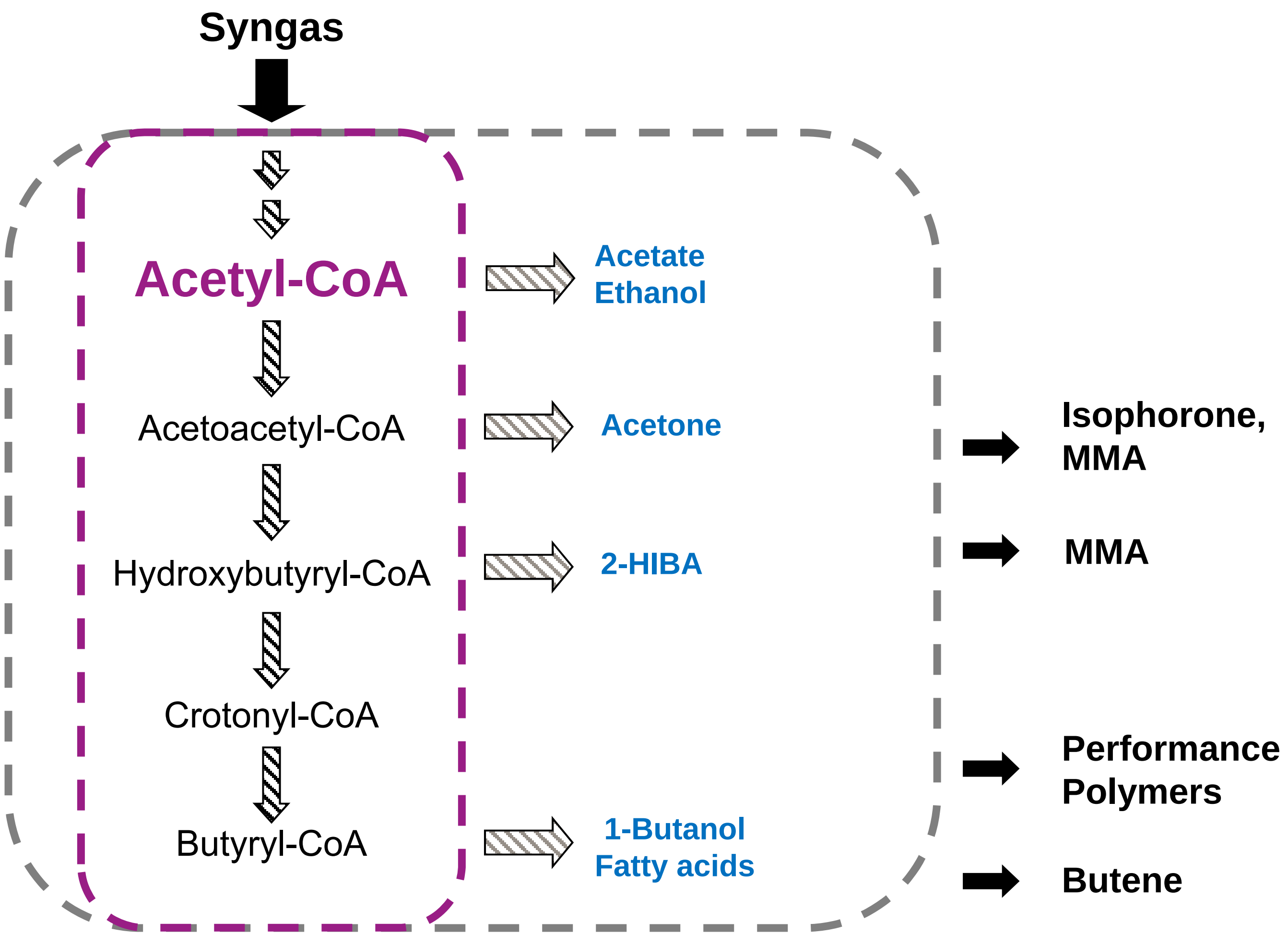
- GMOs are state of the art
- High C-yield
- High value products shown

**Disadvantage:**

- Low hydrogen yield

# Metabolism of syngas based Bacteria

**Key metabolite Acetyl-CoA/Acetat**



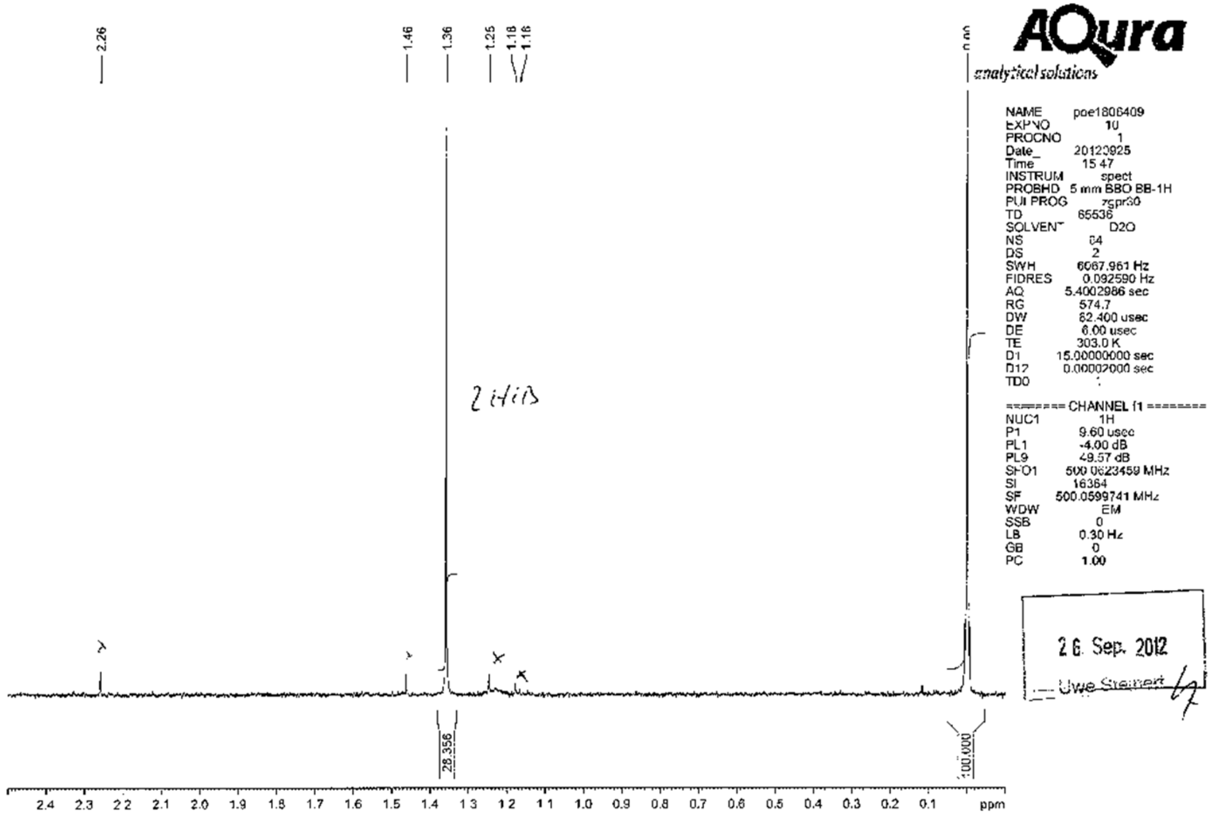

# Syngas fermentation provides high raw material flexibility

- Waste streams of coke oven or steel mills
- Steam reforming or catalytic oxidation of natural gas
- Mixing $CO_2$ waste streams with exogenic $H_2$
- Biomass gasification

**Fermentation of Syngas**

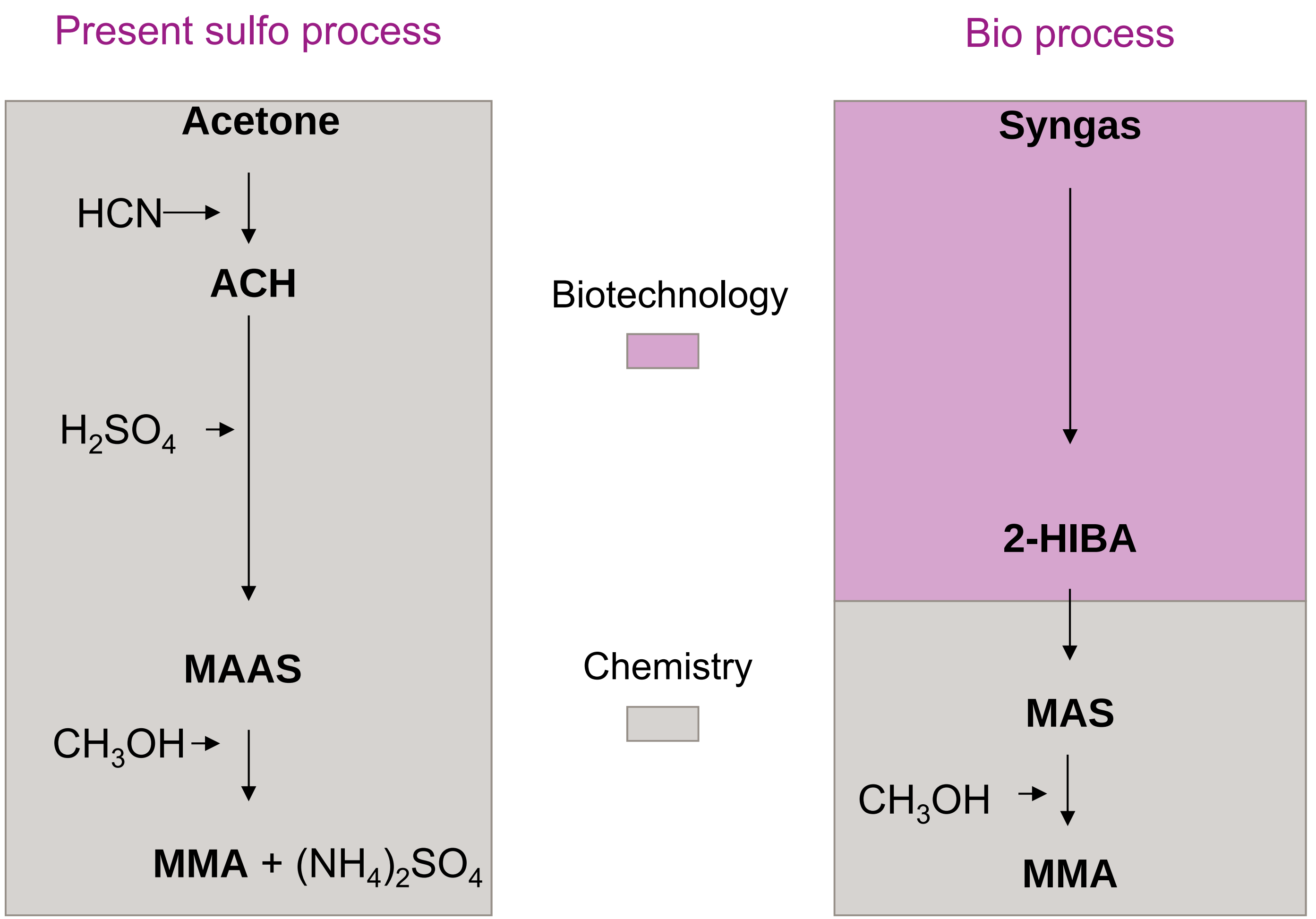
- **Lactic acid, 1,3-Butadiene**
- **Fatty acids**
- **PHB PHA**
- **Butanol, Butanediol**

# The first specialty chemical from syngas fermentation: 2-HIBA

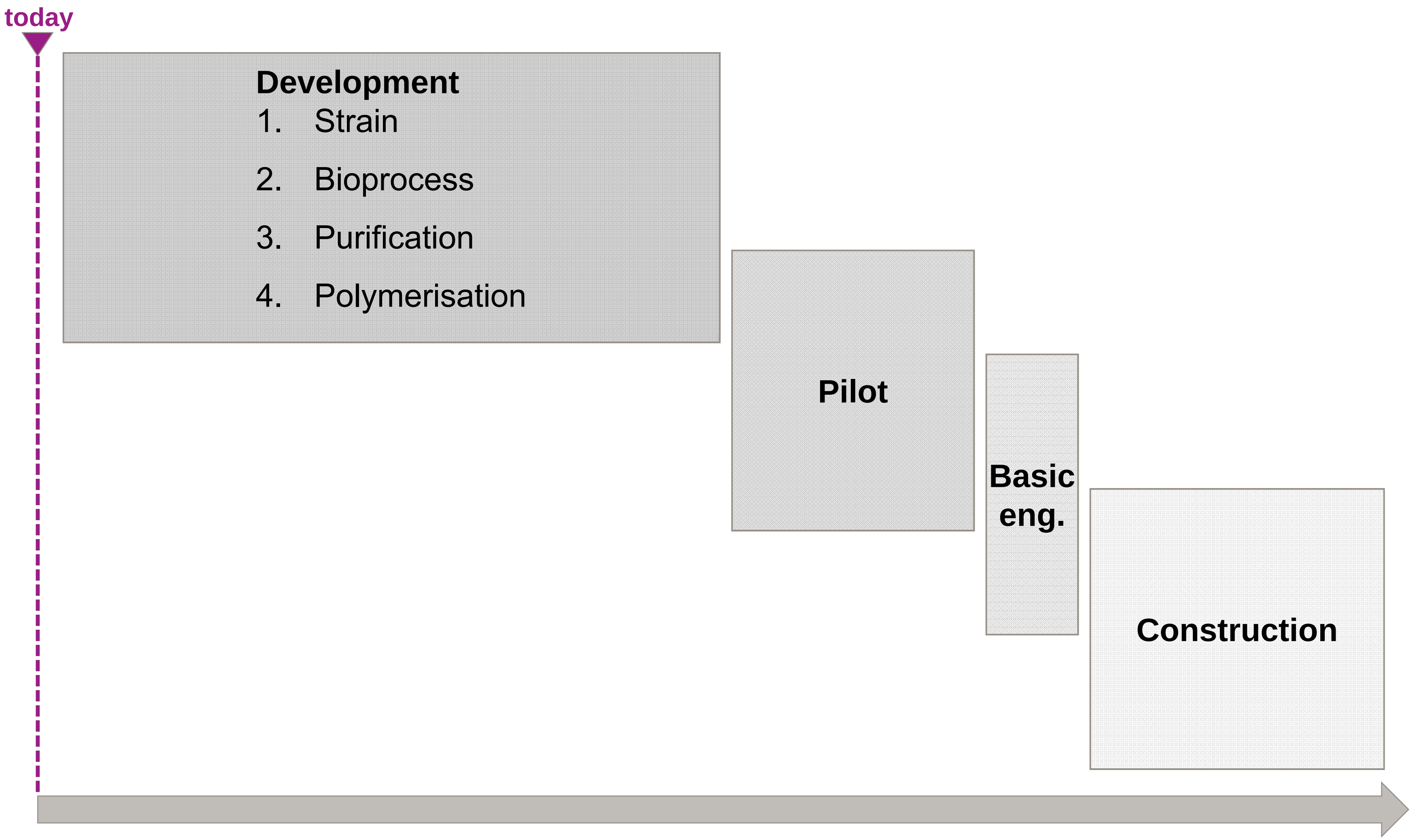



**Genetically modified organism is able to produce highly selective 2-HIBA under autotrophic conditions with syngas.**

# Syngas based biotech process for acrylic glass



# Syngas fermentation: Time to market



# Summary

- Biochemicals from syngas use alternative raw materials significantly increasing feedstock flexibility
- Syngas fermentation opens a new access to speciality chemicals but has some thermodynamic and genetic limitations
- Syngasfermentation provides an attractive approach to invest close to the customers with a very competitive cost position

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