
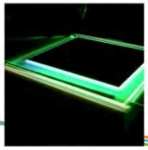

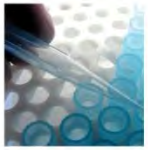

The Antwerp-Rotterdam Rhein Ruhr Chemical Megacluster in transition toward a Smart Specialisation!'

Ludo Diels, VITO, University Antwerp

AIChE, Antwerp, 17 June 2014

Estádio Mineirão, Belo Horizonte, 18.00 h

In 2000 Global chemistry around two centres

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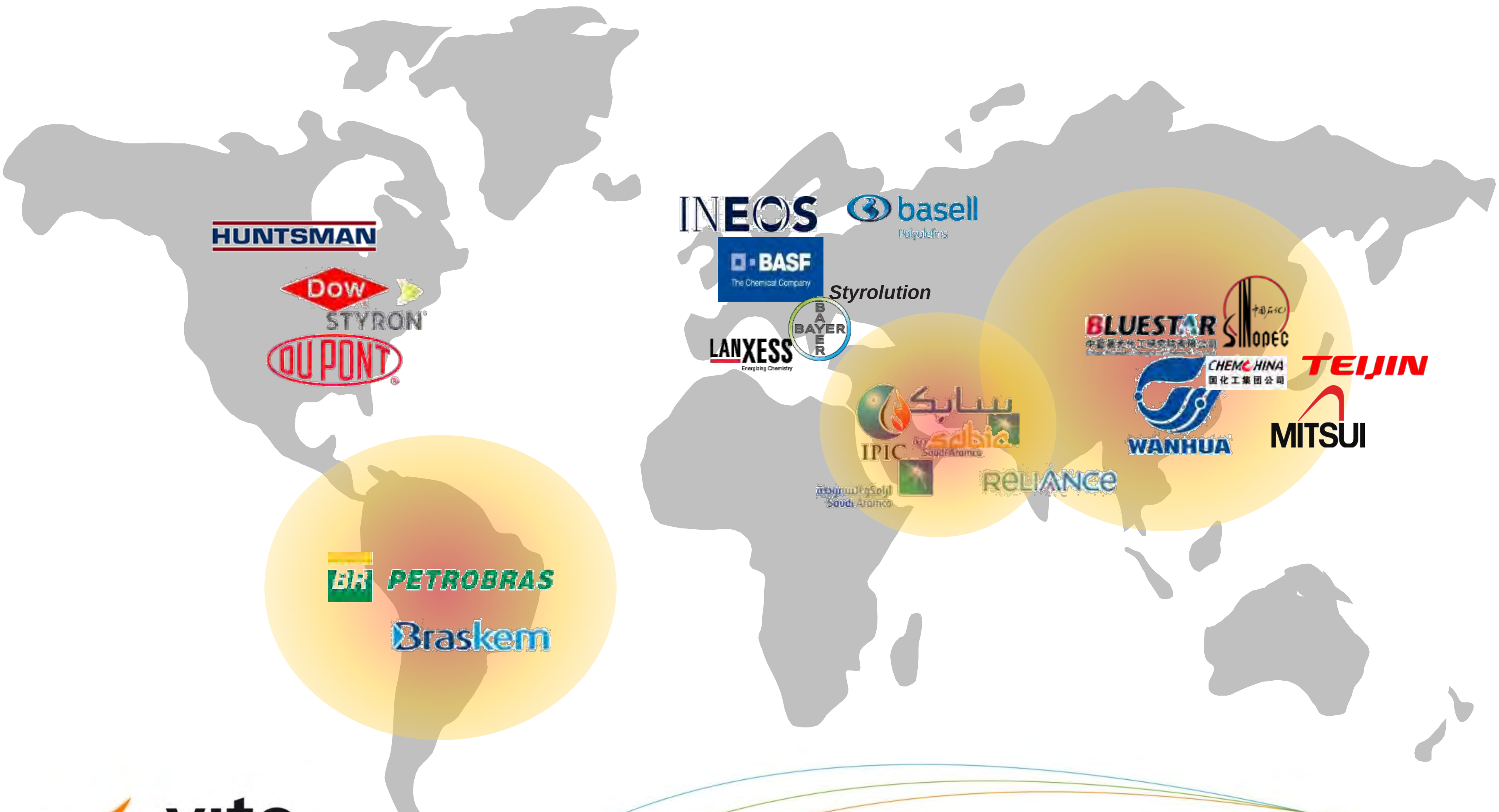
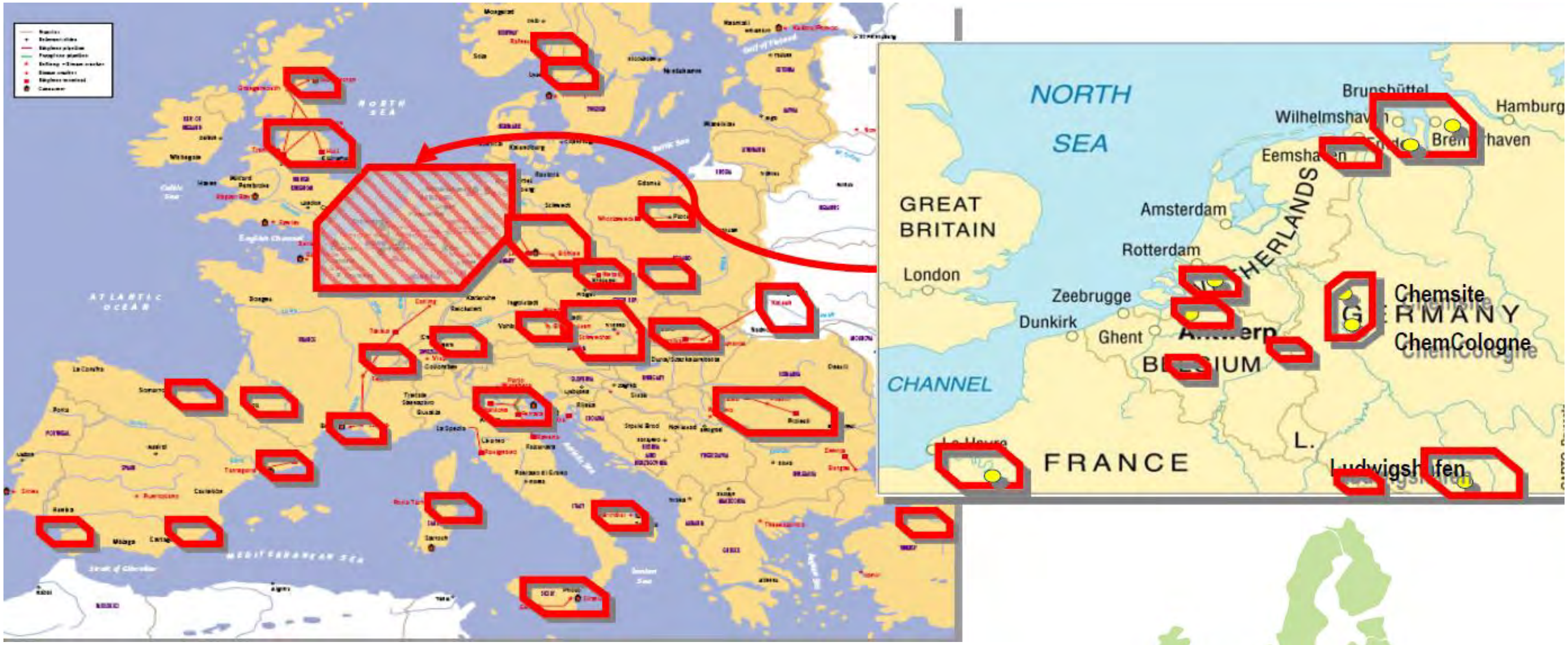
…Then years later, strong competition from BRIC countries



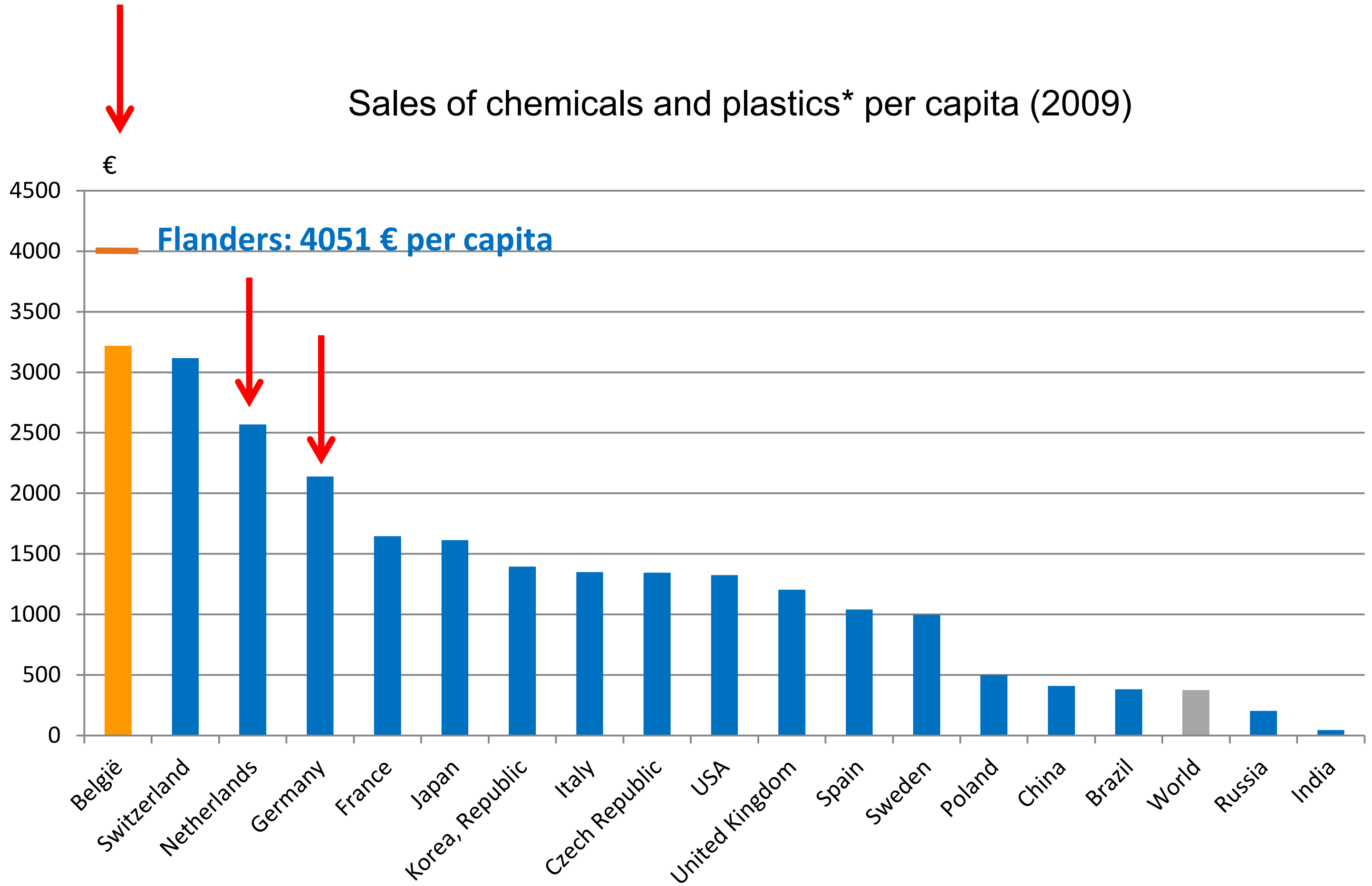
Many chemical clusters, one mega-cluster



Fred du Plessis, (Executive Advisor, Sabic)

Mega-cluster: NL-NRW-Fl

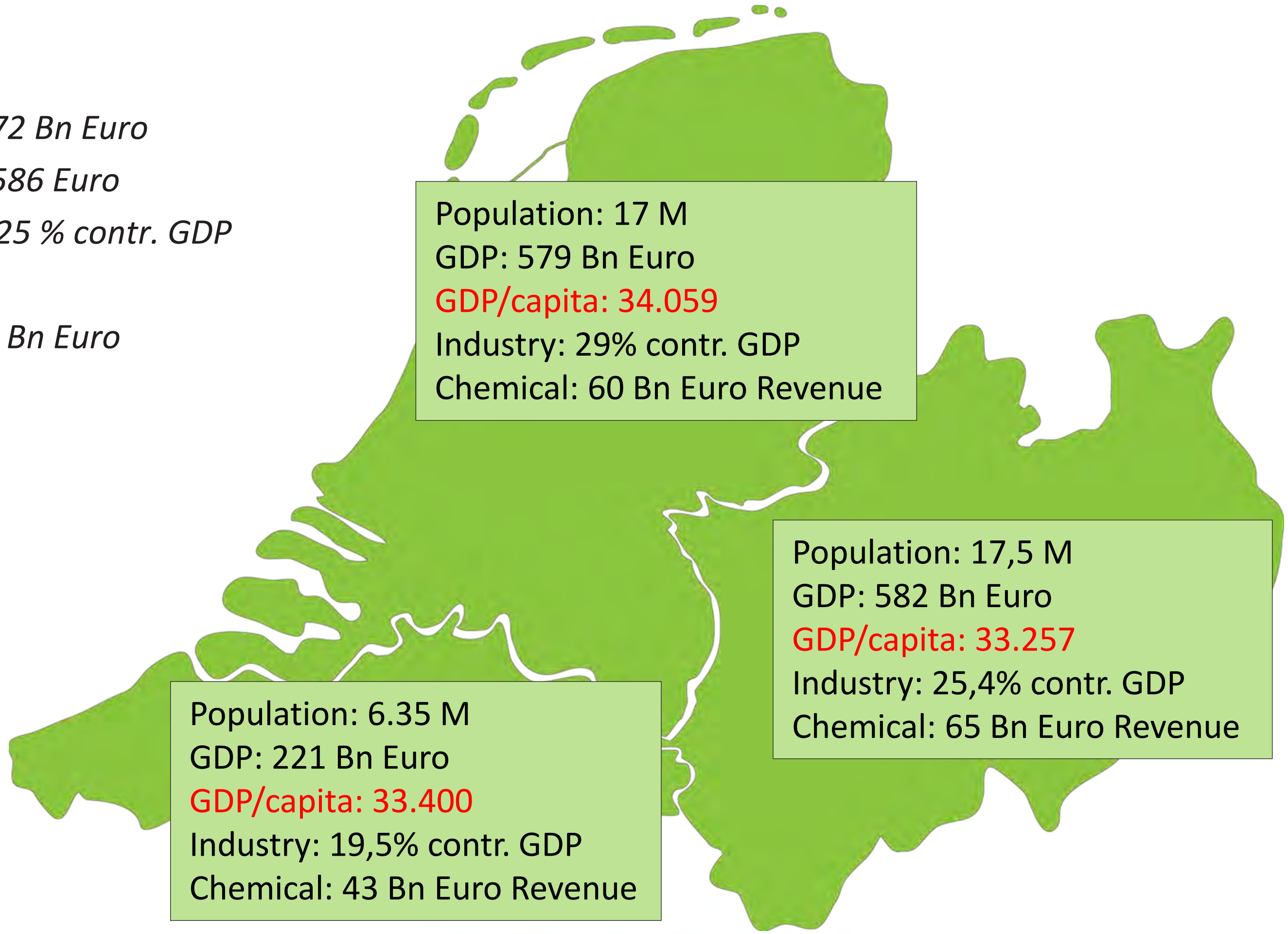
Chemistry per capita



Source: Feri Q12010, NIS
2009 Figures
* exclusive life sciences

The leading industrial mega-cluster

Population: 40,5 M	
GDP:	*1.372 Bn Euro*
GDP/capita:	*33.586 Euro*
Industry:	*ca. 25 % contr. GDP*
Agro&Food: 150 Bn Euro	
Chemical:	*168 Bn Euro*



Mega clusters chemical industry in the world

Outline

» Flanders driven by Chemistry

» Smart specialisation (New feedstock, Process Intensificiation)

» International Initiatives of Clustering and Smart Specialisation

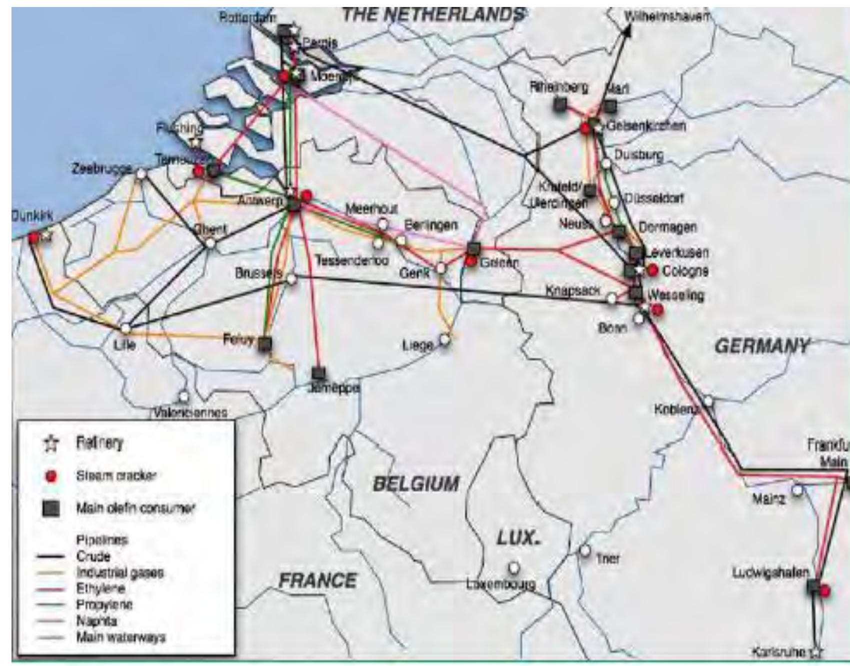
» Conclusions

The pillars of competitiveness (1)

Basic requirements
- Institutions
- Infrastructure & labour
- Macroenomic environment
- Health & primary education

→

Key for
Factor-driven
Economies



The pillars of competitiveness (2)

Basic requirements
- Institutions
- Infrastructure
- Macroenomic environment
- Health & primary education

→ Key for **Factor-driven** Economies

Efficiency enhancers
- Higher education and training
- Goods market efficiency
- Financial market development
- Technological readiness
- Market size

→ Key for **Efficiency-driven** Economies

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Key universities in NRW-Fl-Nl

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Key Knowledge Institutes & Pilot Plants

The pillars of competitiveness (3)

Basic requirements
- Institutions
- Infrastructure
- Macroenomic environment
- Health & primary education

→ Key for **Factor-driven** Economies

Efficiency enhancers
- Higher education and training
- Goods market efficiency
- Financial market development
- Technological readiness
- Market size

→ Key for **Efficiency-driven** Economies

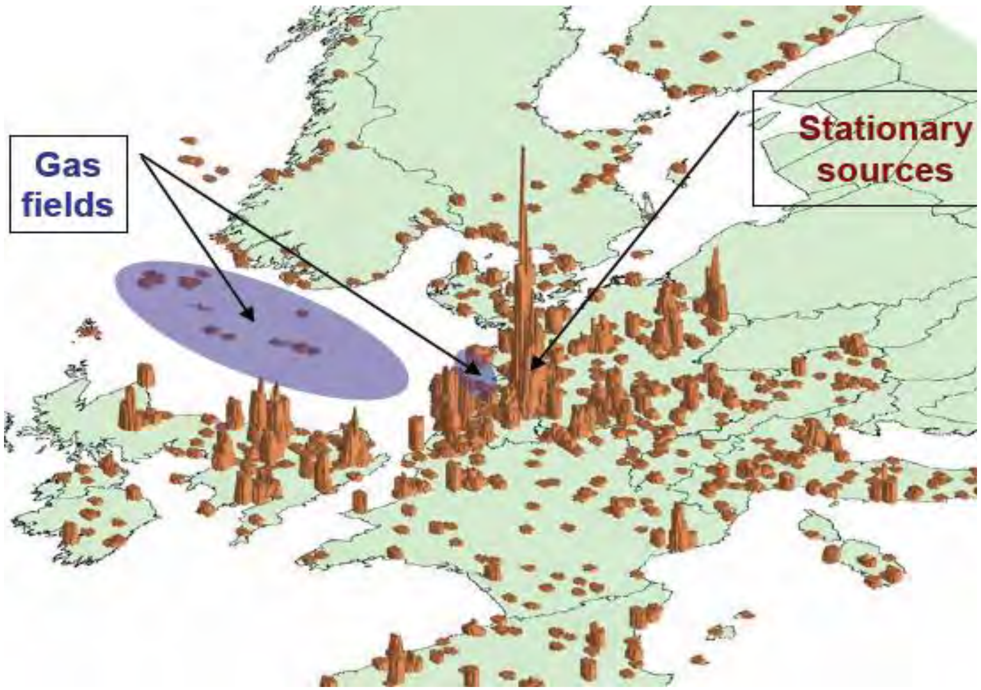
Innovation & sophistication factors
- Business sophistication
- Innovation

→ Key for **Innovation-driven** economies

Source: partially WEF

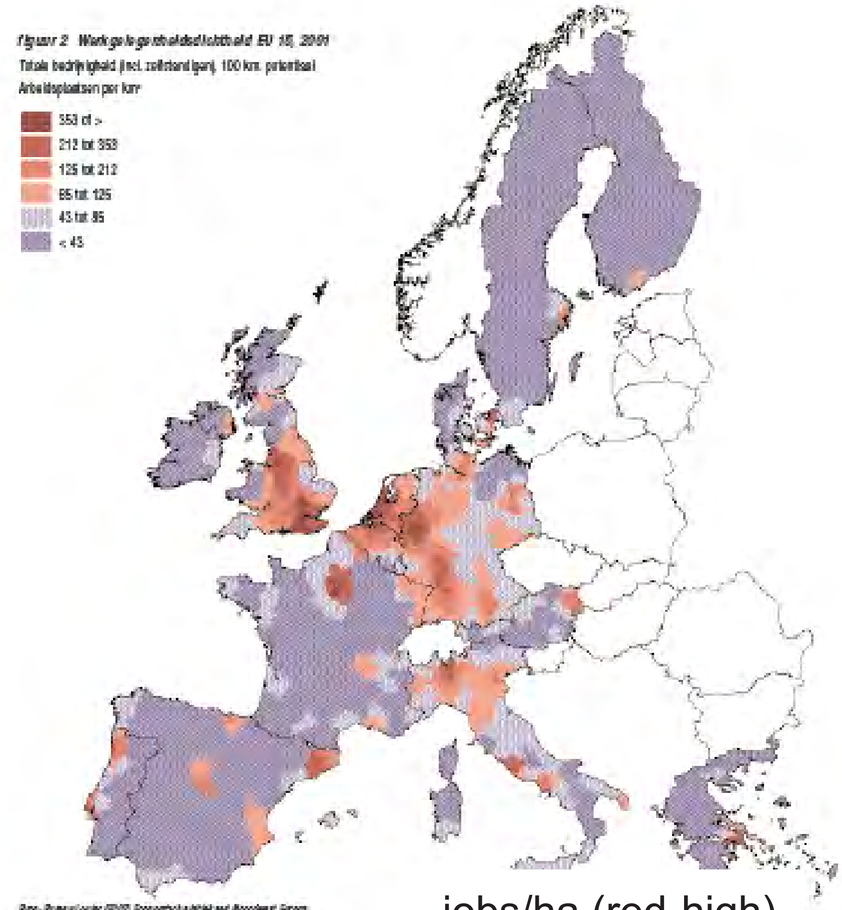
Industrialised and urbanised regions

CO2



CO2/ha/yr

Jobs (Rhine Corridor)



jobs/ha (red-high)

Innovation initatives

Pillars of competitiveness (4)

Basic requirements - Institutions - Infrastructure - Macroenomic environment - Health & primary education	→	Key for **Factor-driven** Economies
Efficiency enhancers - Higher education and training - Goods market efficiency - Financial market development - Technological readiness - Market size	→	Key for **Efficiency-driven** Economies
Innovation & sophistication factors - Business sophistication - Innovation	→	Key for **Innovation-driven** economies
Needs - question factors - Changes in society - Environment & Climate Change	→	Key for **Challenge-driven** economies

Source: partially WEF

Outline

- Flanders driven by Chemistry
- Smart specialisation (New feedstock, Process Intensificiation)
- International Initiatives of Clustering and Smart Specialisation
- Conclusions

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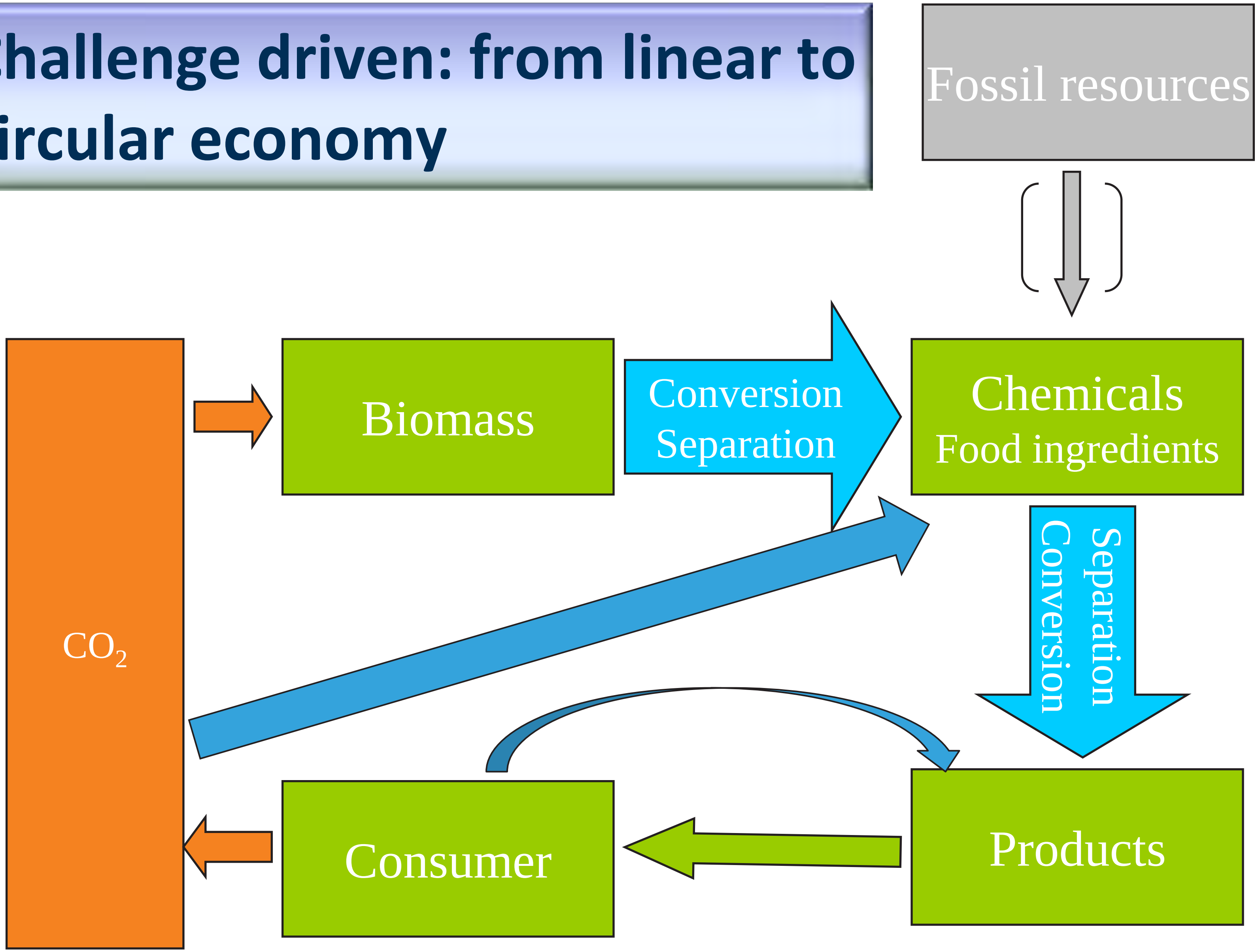
Grand societal challenges

- Food Security
- Clean Energy
- Climate Action
- **Resource Efficiency**
- Secure Societies

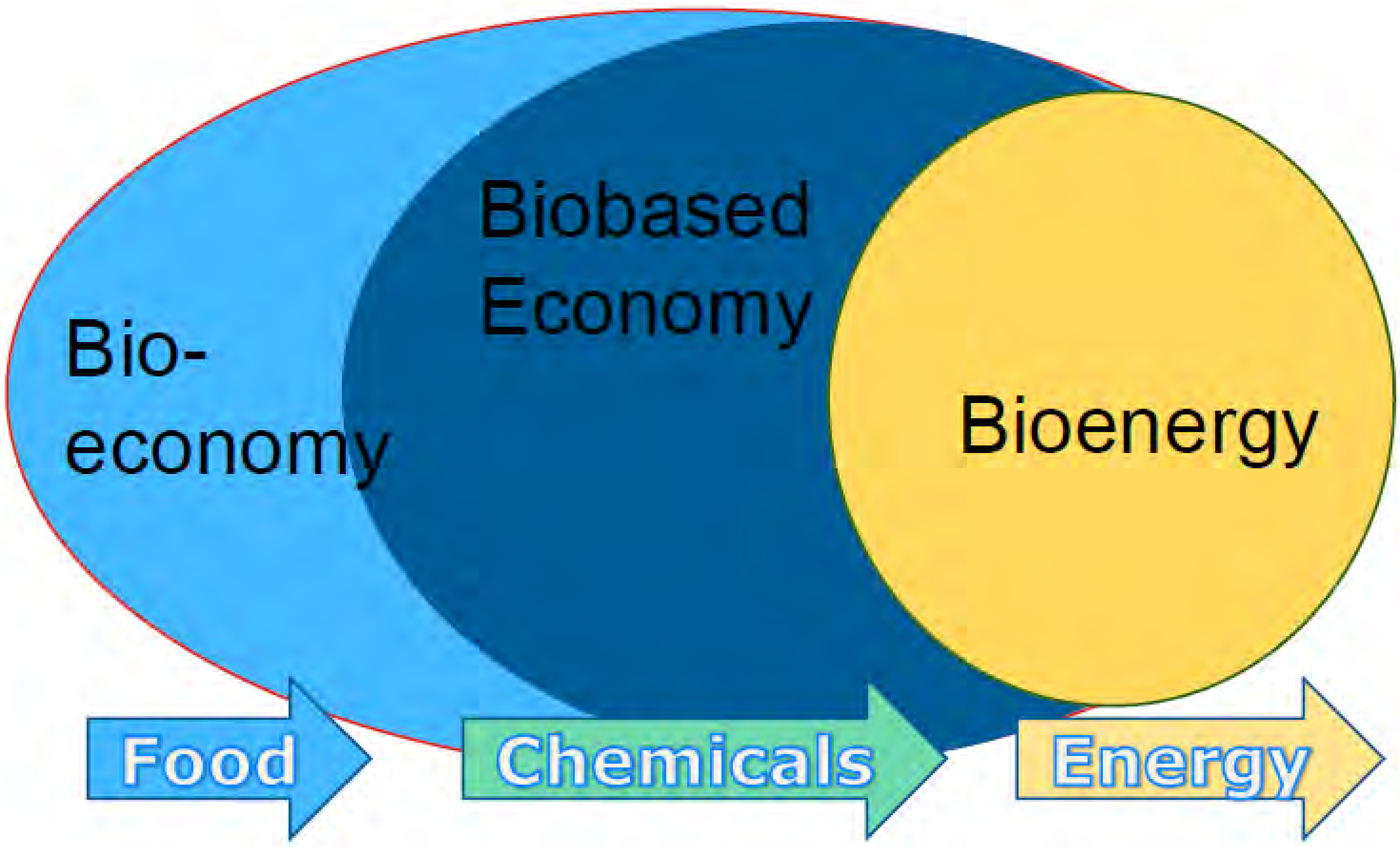
Challenge driven: from linear to circular economy



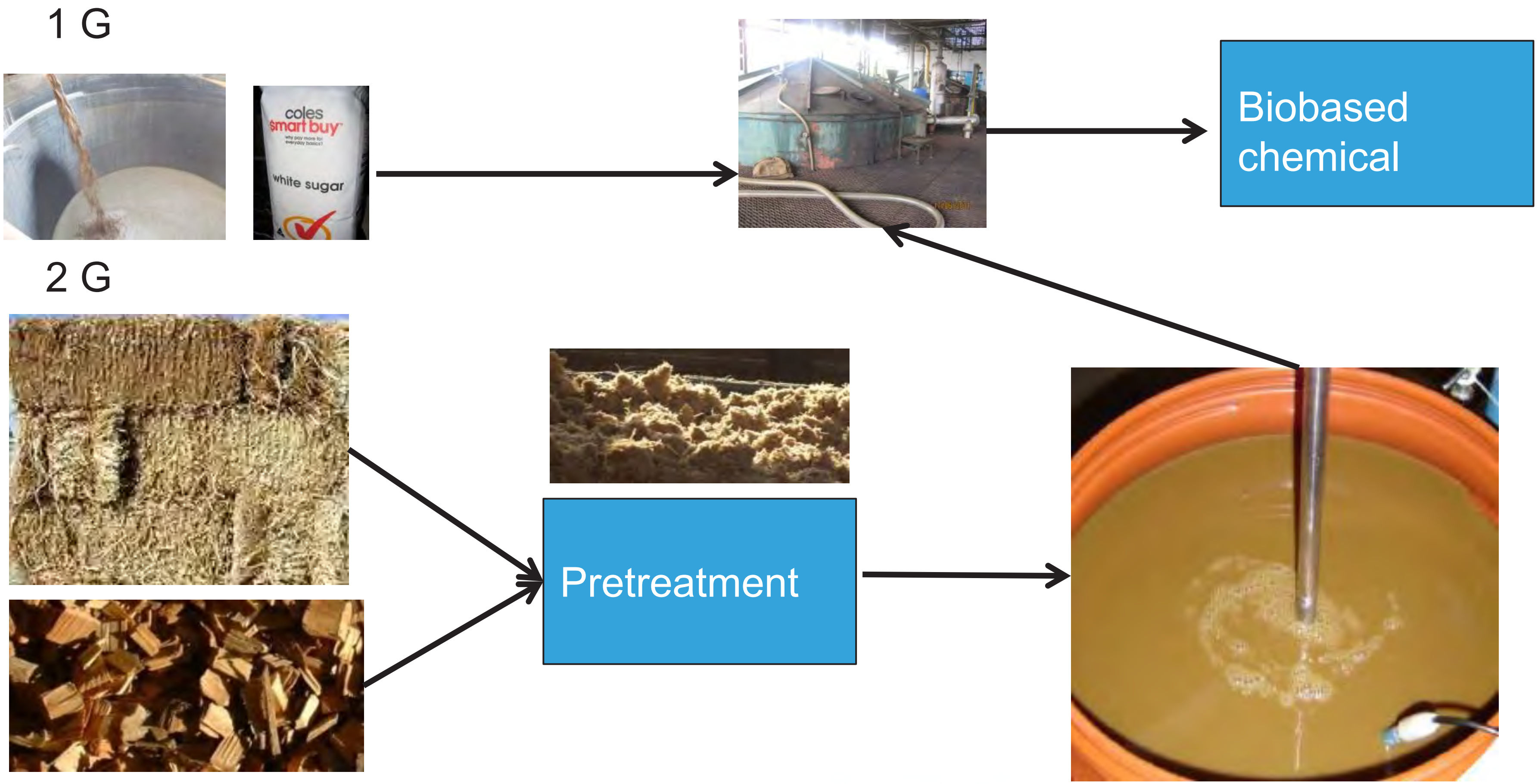
Resource efficiency (1)

- From Linear to Circular Economy
  - New feedstock
    - Biomass & Bioprocess:
      - Biomass: inefficient pretreatment, inefficient hydrolysis
      - Bioprocess: dilute process with high downstream processing costs, high fermentor costs
      - Bioprocess: has a low productivity (inhibition at high product concentrations
    - CO2
      - Relative inert molecule, needs energy to be transformed

What Bio do we mean?

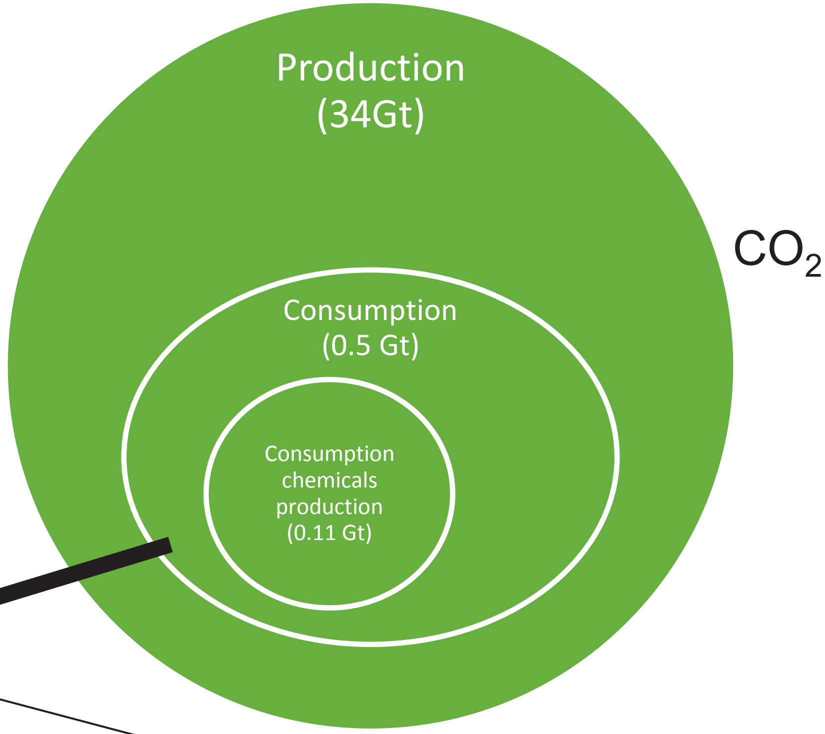


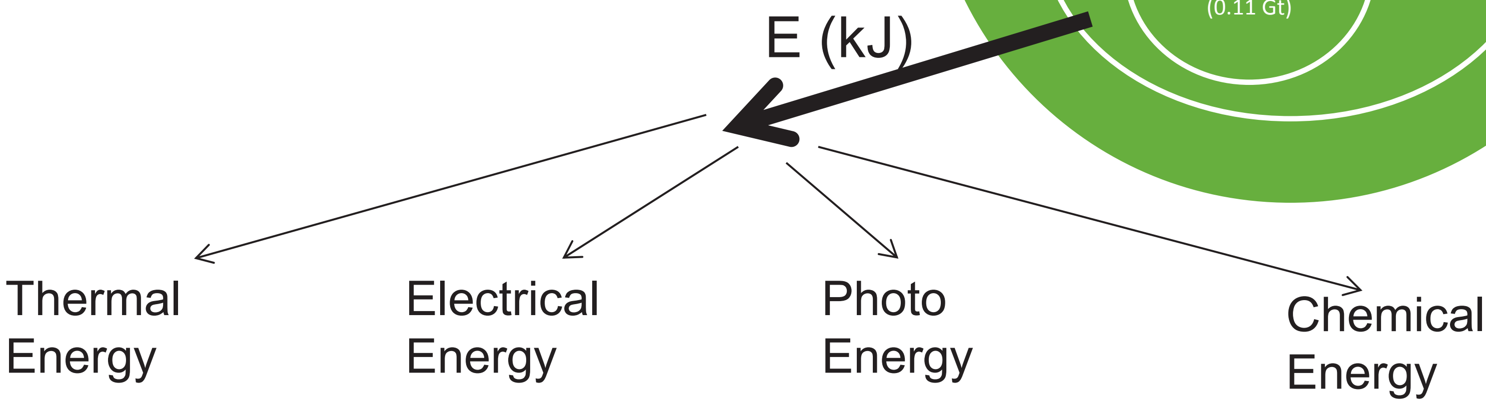
Bioprocesses



Use of CO_2 in chemicals

- Cheap (?) & abundant C1 feedstock
- Non-polar linear molecule, highly thermodynamically stable





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Resource efficiency (2)

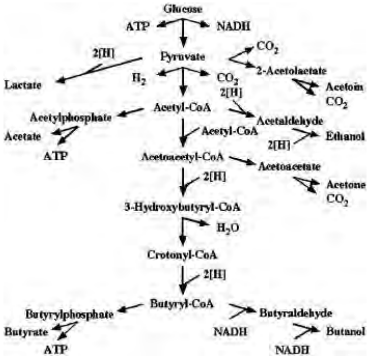
- Process Intensification
  - Process with:
    - Less energy consumption
    - Less waste production
    - Higher efficiency
    - Less side products
    - Higher substrate conversion
    - Less wastewater
    - …..

Challenges

Feedstocks

- *Agricultural waste: straw, corn stover*
- *Industrial waste: sawdust, paper pulp*

Catalyst



- Metabolic engineering of bacteria
- Enzymes
- Catalysts

Process development

- *Continuous fermentation*
- *Cell retention*
- *ISPR*

Down-stream processing

- *Pervaporation*
- *Liquid-liquid extraction*
- *...*

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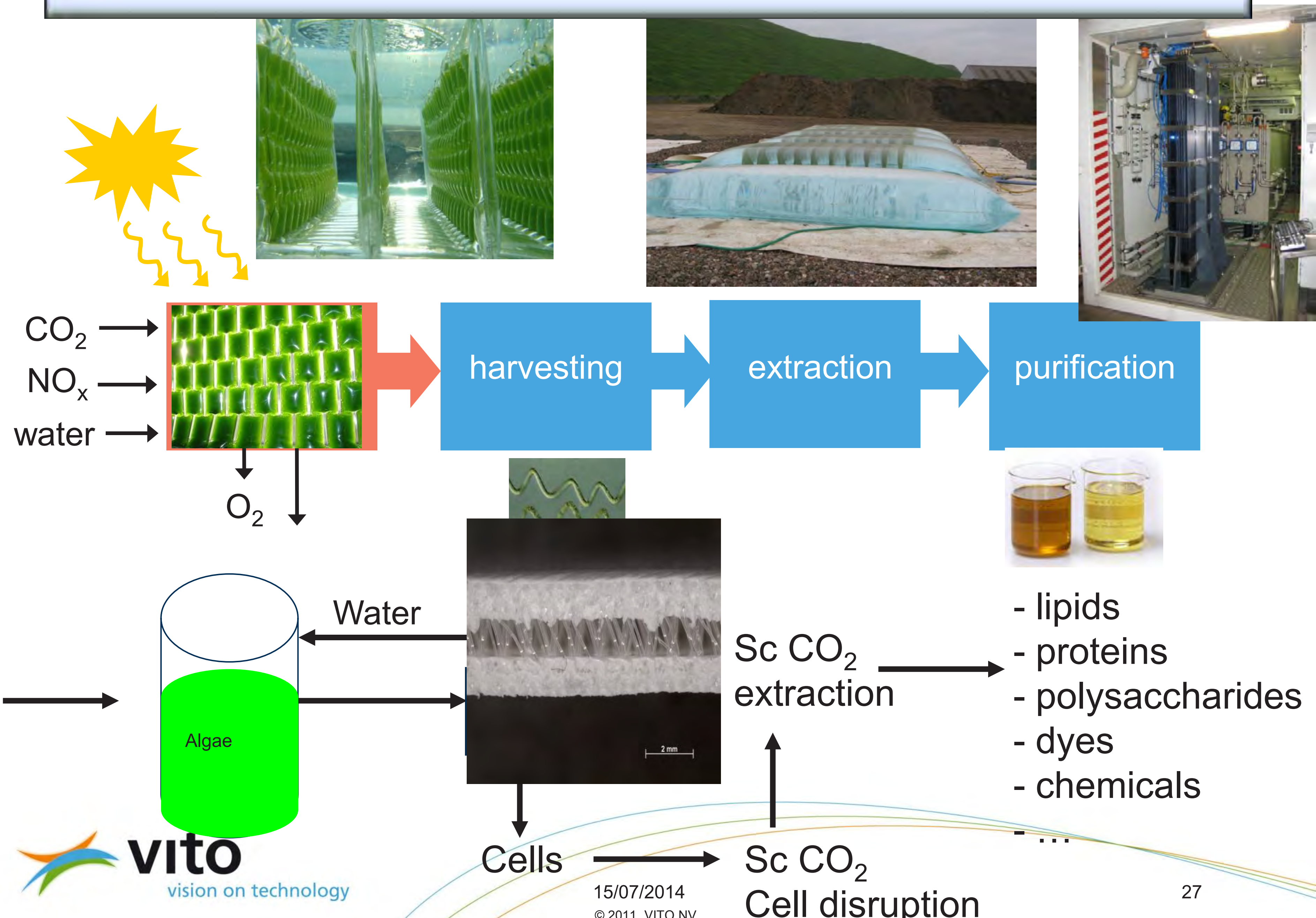
Algae harvesting, disclosure and extraction



Protein extraction (Major component)

Verbinnen/Lintor is a very **large poultry slaughterhouse** with a capacity of approx. 200 000 chickens per day

Mecanically Deboned Meat (MDM)

- Low grade meat
- Low added value
- High cost for transportation (frozen)
- High health risk (cold chain)

→

New application for MDM needed

- Higher added value
- Lower health risk

→

Solution

- Enzymatic conversion to high grade proteins

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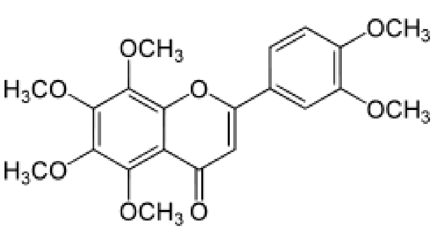
High Value from Citrus Processing Residue (Minor component)

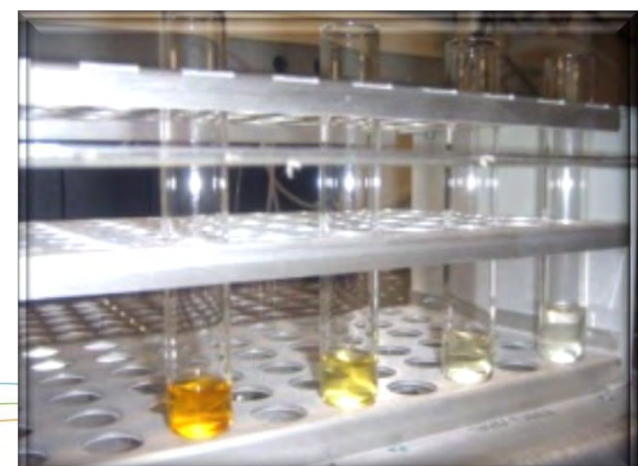
Applications in **Pharmacy**

- Health
- Anti-inflammatory
- Anti-viral
- Cancer treatment

Polymethoxyflavone (PMF) from Citrus Waste extract *

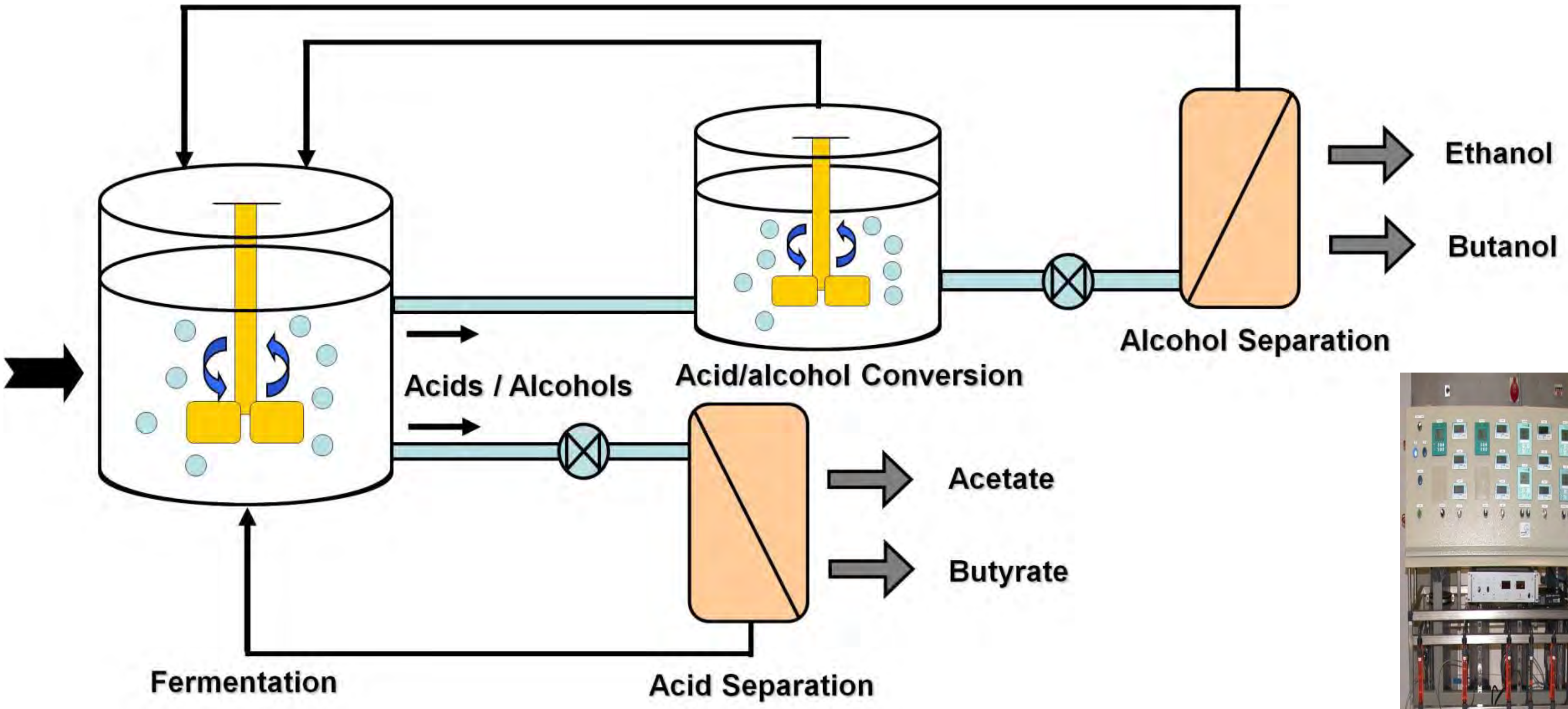
- PMF production (= purification & isolation) with **preparative SFC**
- Pure compound: **300.000 $/g**





* Wang, Presentation at SFC 2009

Wastewater + waste transformation into chemicals



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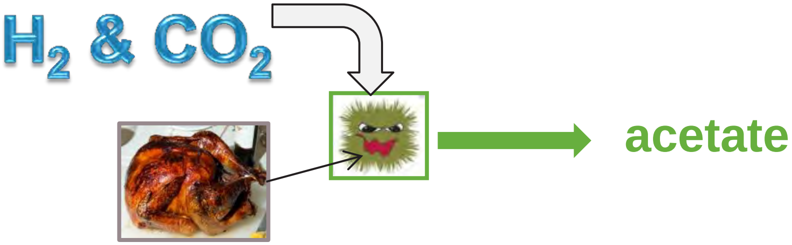
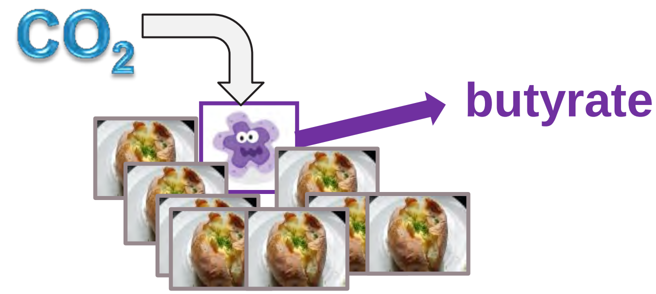
15/07/2014

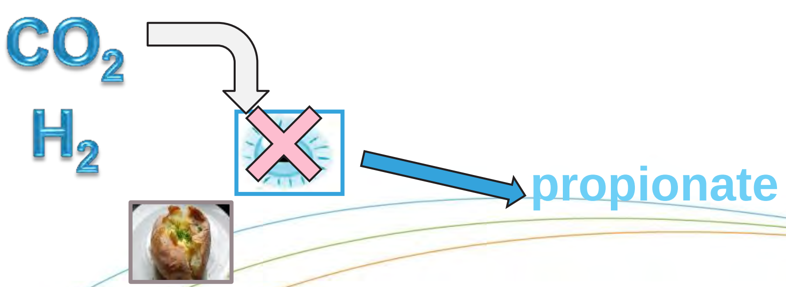
Directing fermentation towards to a product

- Acetate →
  - pH_2 & pCO_2 together
  - Protein rich substrate



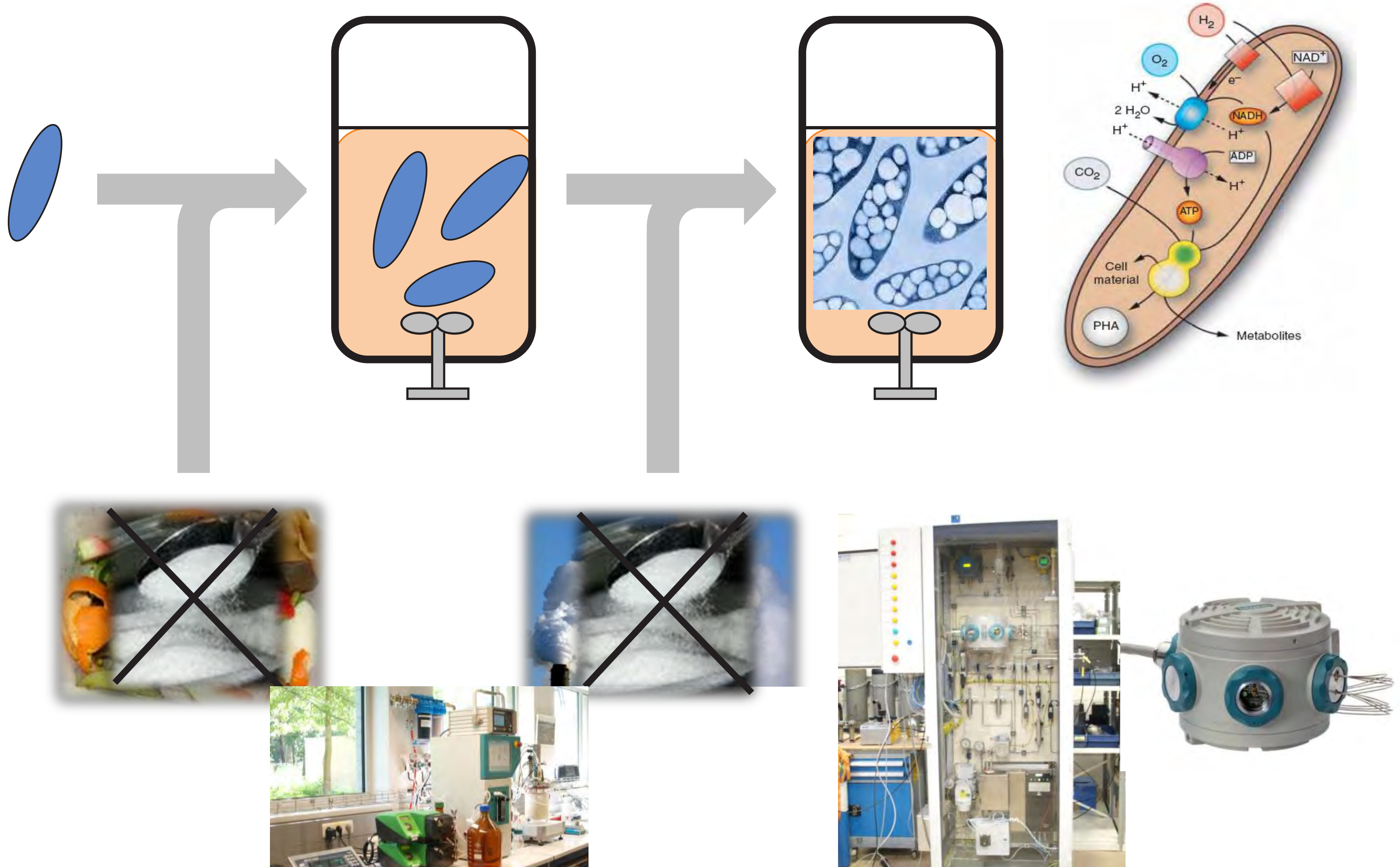


- Butyrate →
  - pCO_2 with carbohydrate rich substrate
  - High substrate concentration without headspace addition
- Propionate →
  - Without headspace manipulation under low substrate feeding

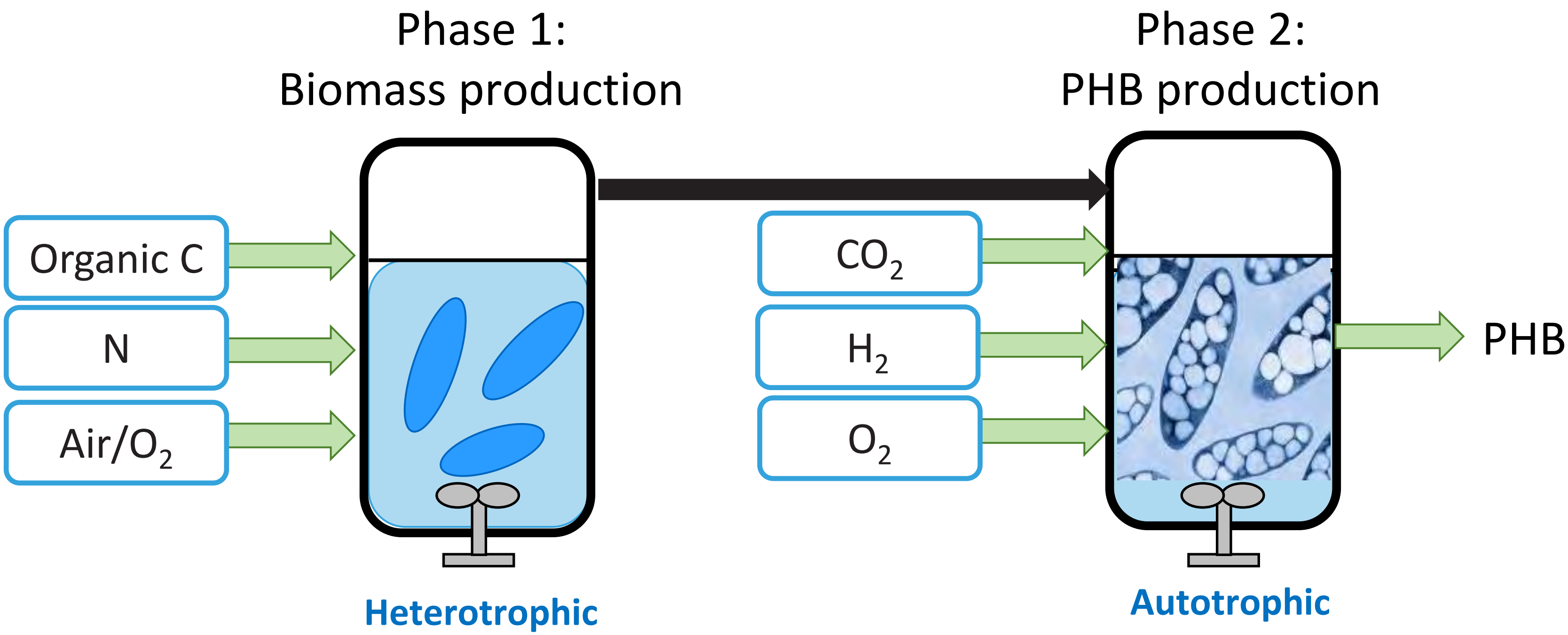


Heterotrophic biomass production – autotrophic PHA production

Biomass production **PHA production**



Biosynthesis of PHB from CO_2 at VITO



Waste glycerol

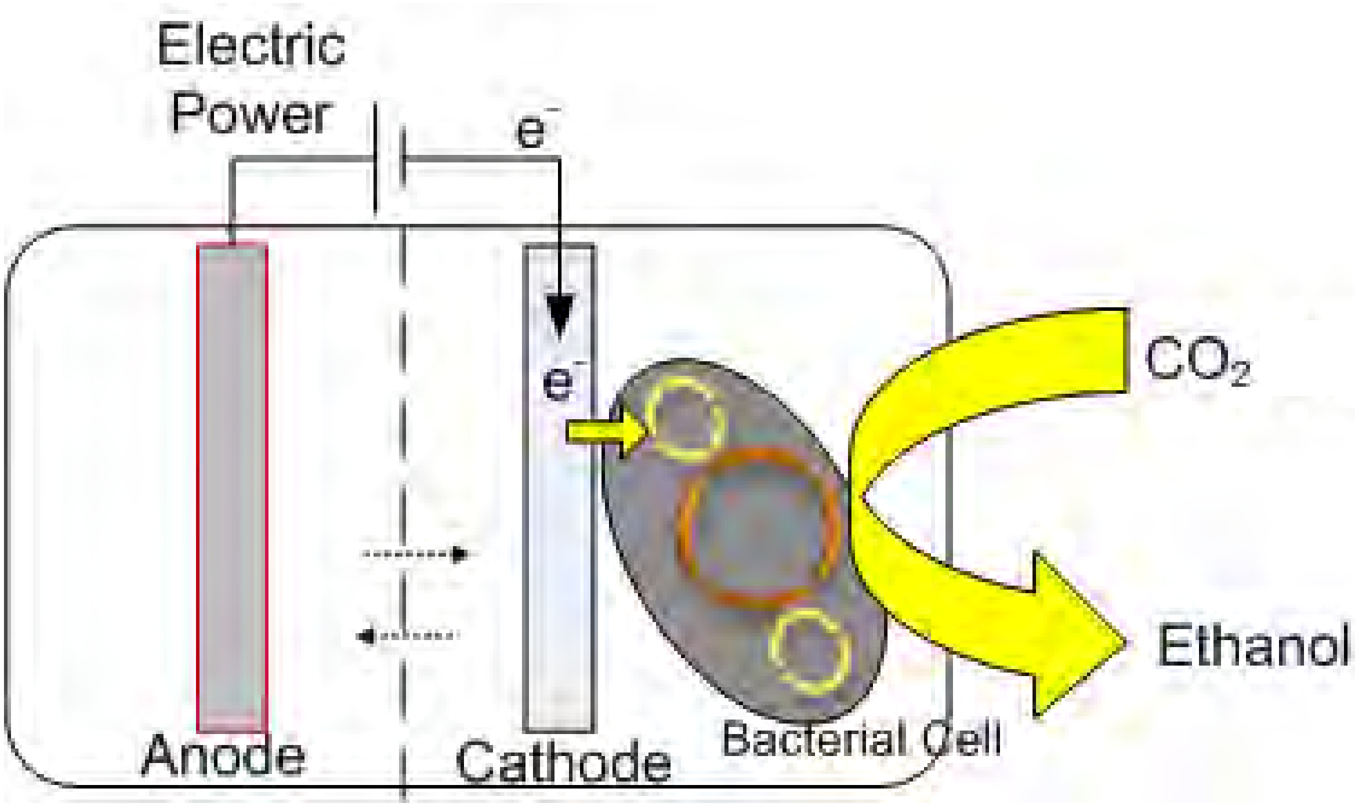
Waste gas

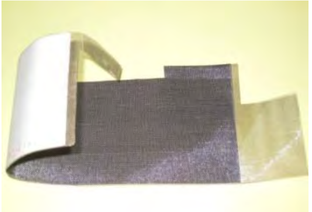
PHB production using pure substrates

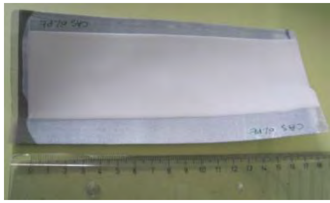
Substrate	DCW (g/L) at onset N limitation	DCW (g/L)	PHB (g/L)	PHB content (%)	PHB productivity (g/L.h) – phase 2	Reference
Glucose - $CO_2/H_2/O_2$ 8.16/67.4/2.8	5	21	16	74	0.249	VITO
Glucose - $CO_2/H_2/O_2$ 10.42/86/2.8	15	27	12	44	0.168	VITO
Glucose $CO_2/H_2/O_2$ 10.42/86/2.8	18	32	15.2	47	0.201	VITO
Glucose $CO_2/H_2/O_2$ 10.42/86/2.8	42	29	0.12	0.4	-	VITO

- PHB concentration and PHB content decreased with increasing biomass concentration
- At high DCW, no PHB was produced.
  - Gas limitation?
  - Hydrogenase enzyme depressed by substrate?

Bio-electrochemical technology for bioethanol Production





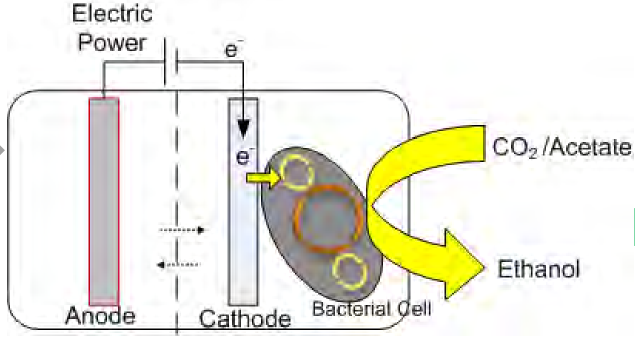


Integration of atmospheric plasma technology in existing energy and chemical infrastructure

Greenhouse gases
CO_2

Electricity

- Peak shaving
- Recovery of process heat
- Grid balancing, rest energy from renewable sources
- Solar energy for synthesis of solar fuels and solar chemicals



Base chemicals & liquid fuels

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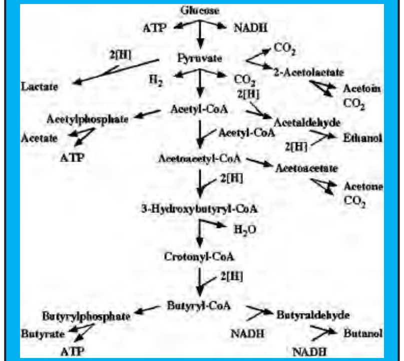
Challenges

Feedstocks

- *Agricultural waste: straw, corn stover*
- *Industrial waste: sawdust, paper pulp*

Catalysis



- Bacteria
- Enzymes
- Catalysts

Process development

- *Continuous fermentation*
- *Cell retention*
- *ISPR*

Down-stream processing

- *Pervaporation*
- *Liquid-liquid extraction*
- *...*

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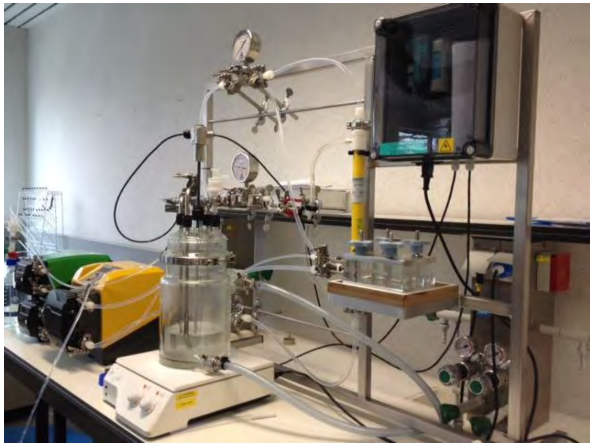
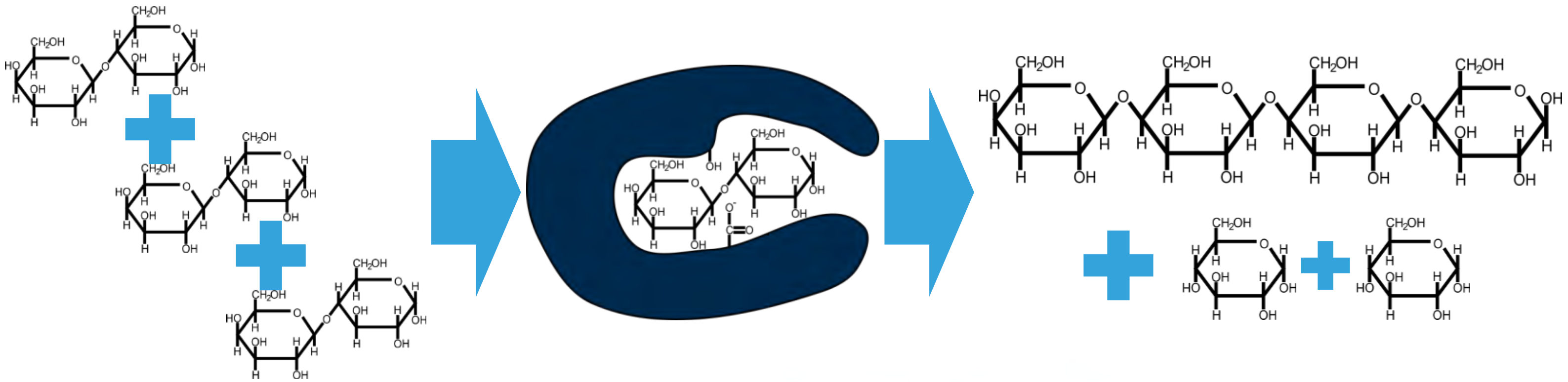
Enzyme reuse and increased stability

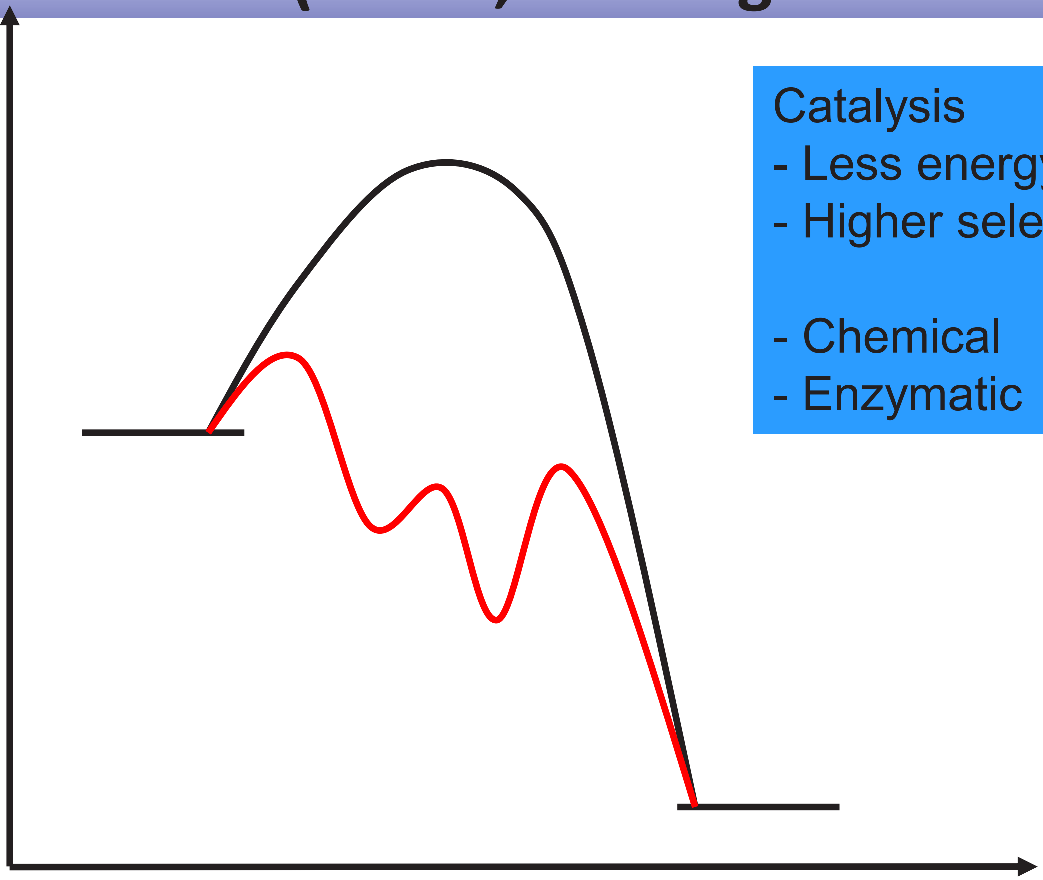


- Enzymatic Reactors (ERs): enzyme retention by immobilization
  - **Advantage**: higher stability of enzyme and thus specific productivity
  - **Challenge:** (1) cheap & reusable carrier and (2) good immobilisation technique

Example: Prebiotic GOS production using enzymatic conversion of lactose

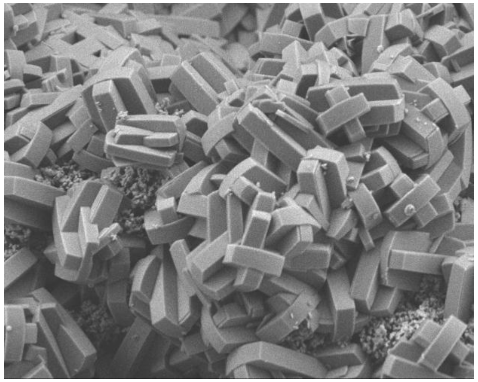


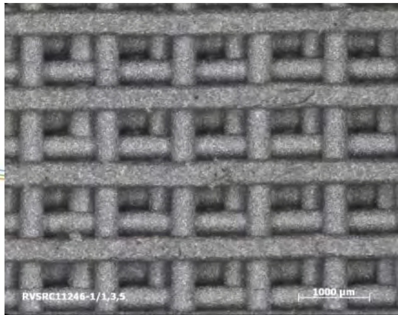
Maximize the effectiveness of inter and intramolecular reactions (homo, heterogenous catalysts)



Catalysis
- Less energy
- Higher selectivity

- Chemical
- Enzymatic





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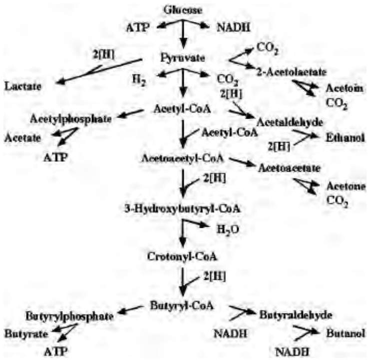
Challenges

Feedstocks

- *Agricultural waste: straw, corn stover*
- *Industrial waste: sawdust, paper pulp*

Metabolic engineering



- Strain engineering
- Enzymes
- Catalysts

Process development

- *Continuous fermentation*
- *Cell retention*
- *ISPR*

Down-stream processing

- *Pervaporation*
- *Liquid-liquid extraction*
- *...*

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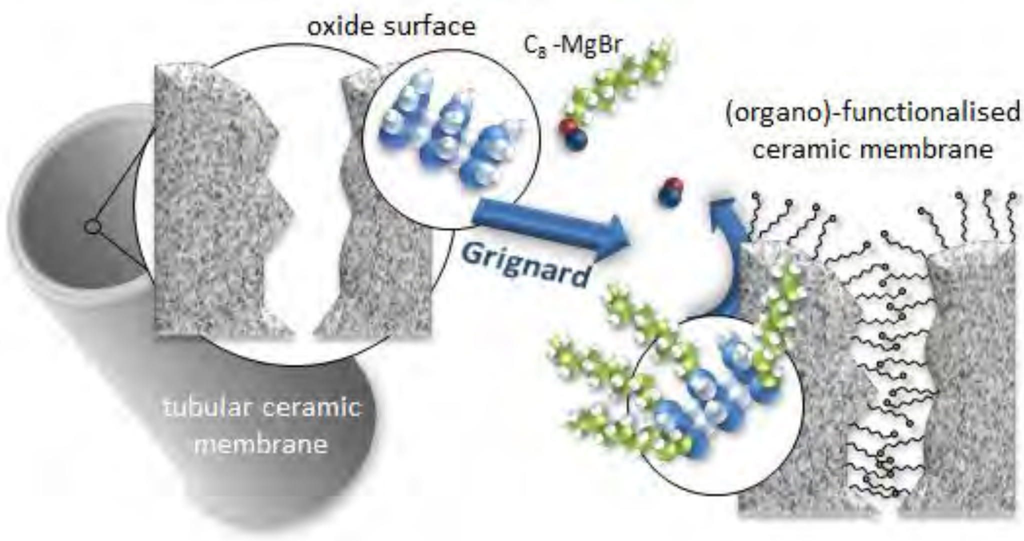
Post modified ceramic membranes for OSN applications (homogeneous cata recovery)

Combine **Intrinsic (thermo)chemical stability of ceramic membranes** **with** **Good flux performance of polymeric membranes**

Via an unique versatile grafting method with various organic functional groups, like for instance alkyls, phenyls, or amines

Improved membrane separation properties by extra affinity-based selectivity factor in solvent filtration.

Opens the path for preparing a wide range of novel membranes with given surface functionalities



- European patent application EP 09 155 686.0
- P. Van Heetvelde et al., Chem. Commun., **2013**, *49*, 6998-7000.
- S. Rezaei Hosseinabadi et al., **2013**, Accepted for publication in *J. Membr. Sc.*

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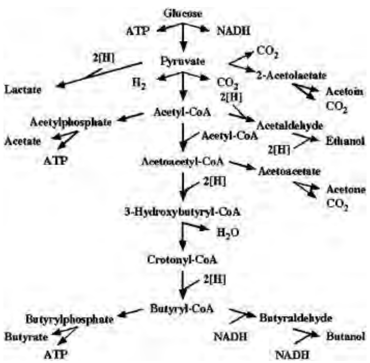
Challenges

Feedstocks

- *Agricultural waste: straw, corn stover*
- *Industrial waste: sawdust, paper pulp*

Metabolic engineering



- *E. coli*
- *S. cerevisiae*
- *P. putida*

Process development

- *Continuous fermentation*
- *Cell retention*
- *ISPR*

Down-stream processing

- *Pervaporation*
- *Liquid-liquid extraction*
- *…*

MemProRec

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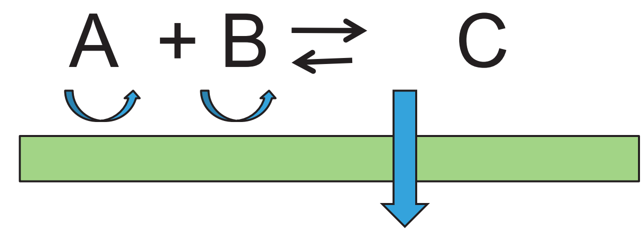
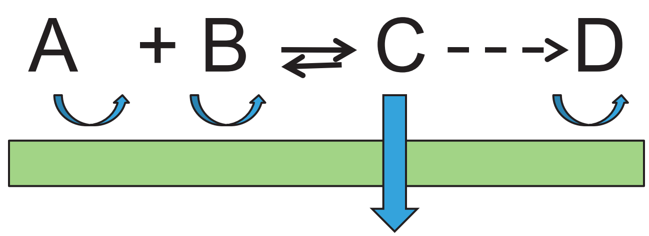
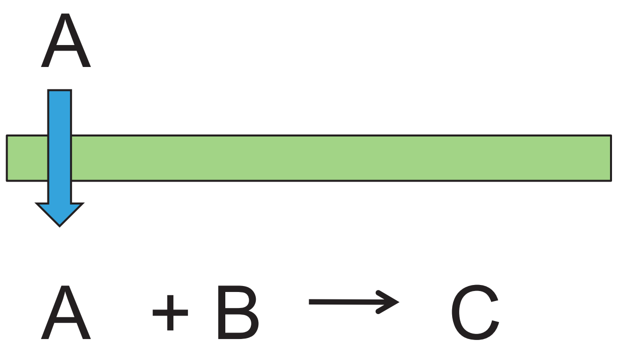
Process intensification: In situ product recovery



Change in equilibrium



Avoiding further reactions



Dosing chemicals to control the right reaction

Ultra-performing OPV membranes

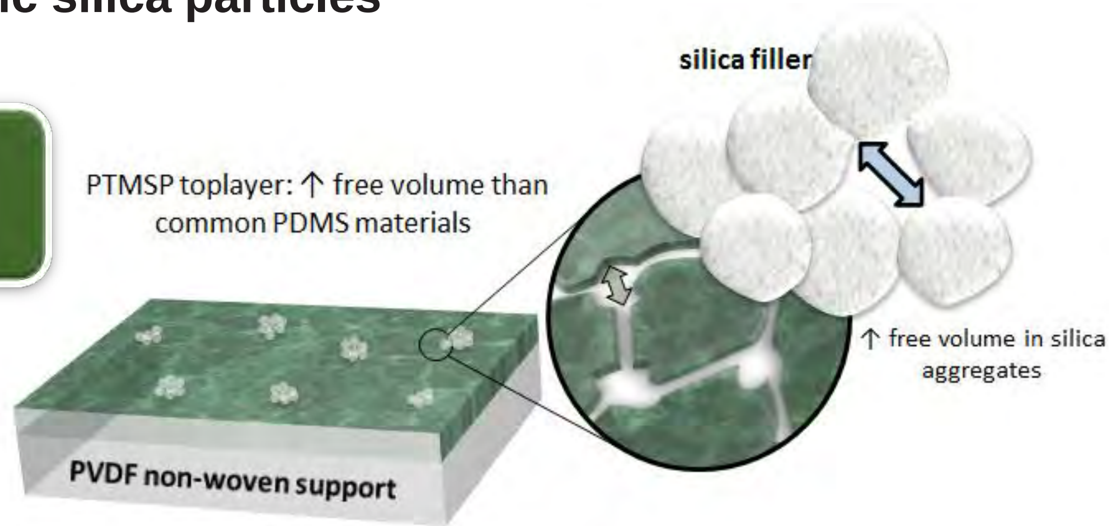
Make use of PTMSP superior intrinsic properties

- Extremely high free volume fraction and inherent nanoporosity
- Solubility controlled separation capacity and pronounced hydrophobicity

+ high free volume, hydrophobic silica particles

Increased flux performance and improved separation characteristics

Thermal crosslinking for application in demanding solvent:water mixtures

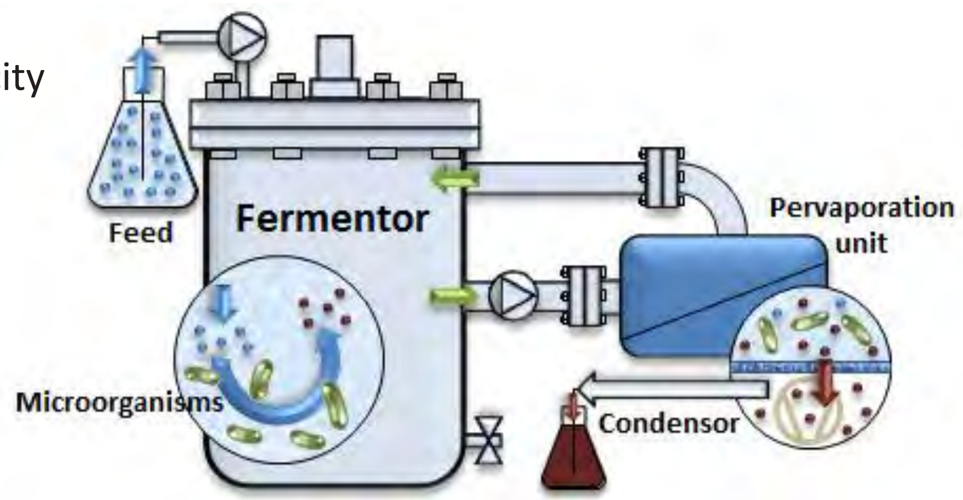


- S. Claes et al., *J. Membr. Sci.*, **2010**, *351*, 160-167.
- K. De Sitter et al., *J. Membr. Sci.*, **2006**, *278*, 83-91.
- S. Claes et al., *J. Membr.Sc.*, **2012**, 389, 265-271.
- S. Claes et al., *J. Membr.Sc.*, **2012**, *389*, 459-469.

OPV for *in-situ* Product Recovery

Traditionally batchwise

- Low product concentrations due to product toxicity
- Low productivity, while high cost of substrates
- High purification costs



Integration with OPV

- Continuous, selective product withdrawal from reaction medium from 20 $g.L^{-1}$ to >200 $g.L^{-1}$
- Low energy demanding separation technique

Continuous process

- Productivity enhancement by removal of product inhibition from 0.36 $g.L^{-1}.h^{-1}$ to 1.13 $g.L^{-1}.h^{-1}$
- Concentrated feedstocks can be fermented
- Energy gains from complementation of distillation with efficient primary work-up step

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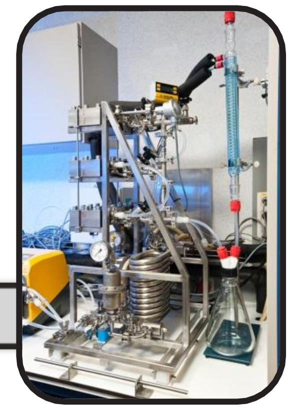
OPV for *in-situ* Product Recovery

Lab-scale demonstration unit @VITO

Biobutanol production from glucose fermentation :
- Two-stage continuous process, chemostat operation
- Fermentation divided in acidogenic and solventogenic state
- Synthetic medium

Coupled with PERVAPORATION Membrane Technology:



- Directly coupled to solventogenic fermentor
- PDMS and PTMSP (home-made) membranes

- Successful continuous fermentation during 475 h
- Feedstock concentration increased to 126 g.L^{-1} glucose
- Permeate enriched to 57-195 g.L^{-1} total solvents

W. Van Hecke et al., *Bioresource Technol.*, **2012**, *111*, 368-377.
W. Van Hecke et al., *Bioresource Technol.*, **2013**, *129*, 421-429.
M.F.S. Dubreuil et al., *J.Membr.Sc.*, **2013**, *447*, 134–143.

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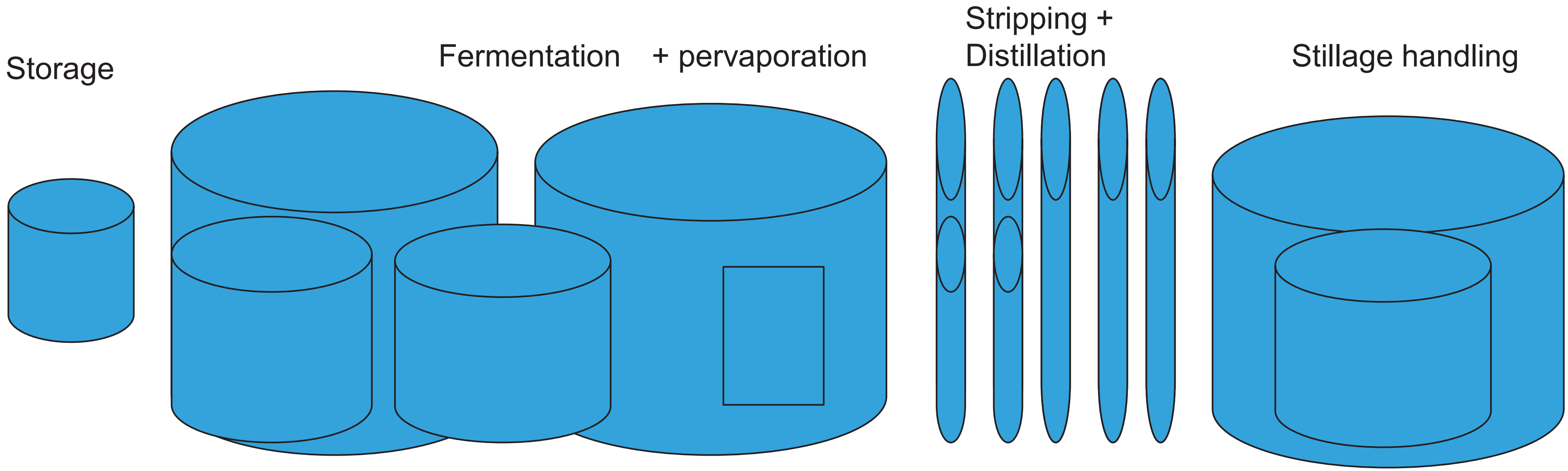
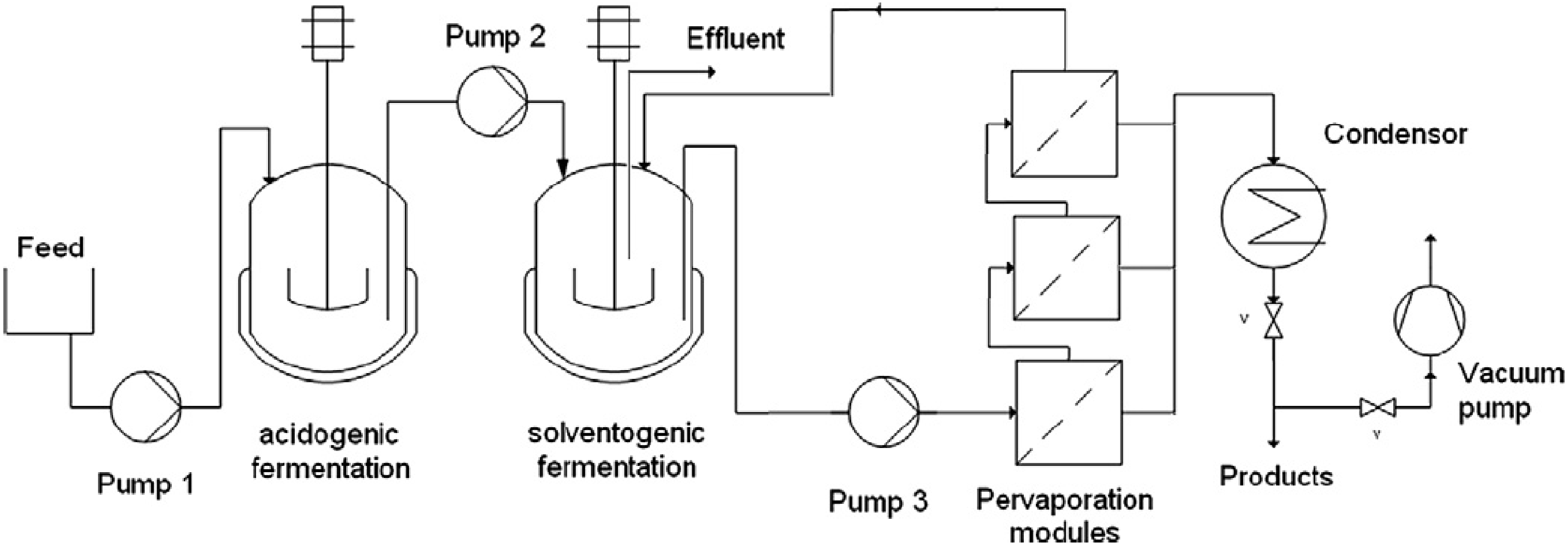
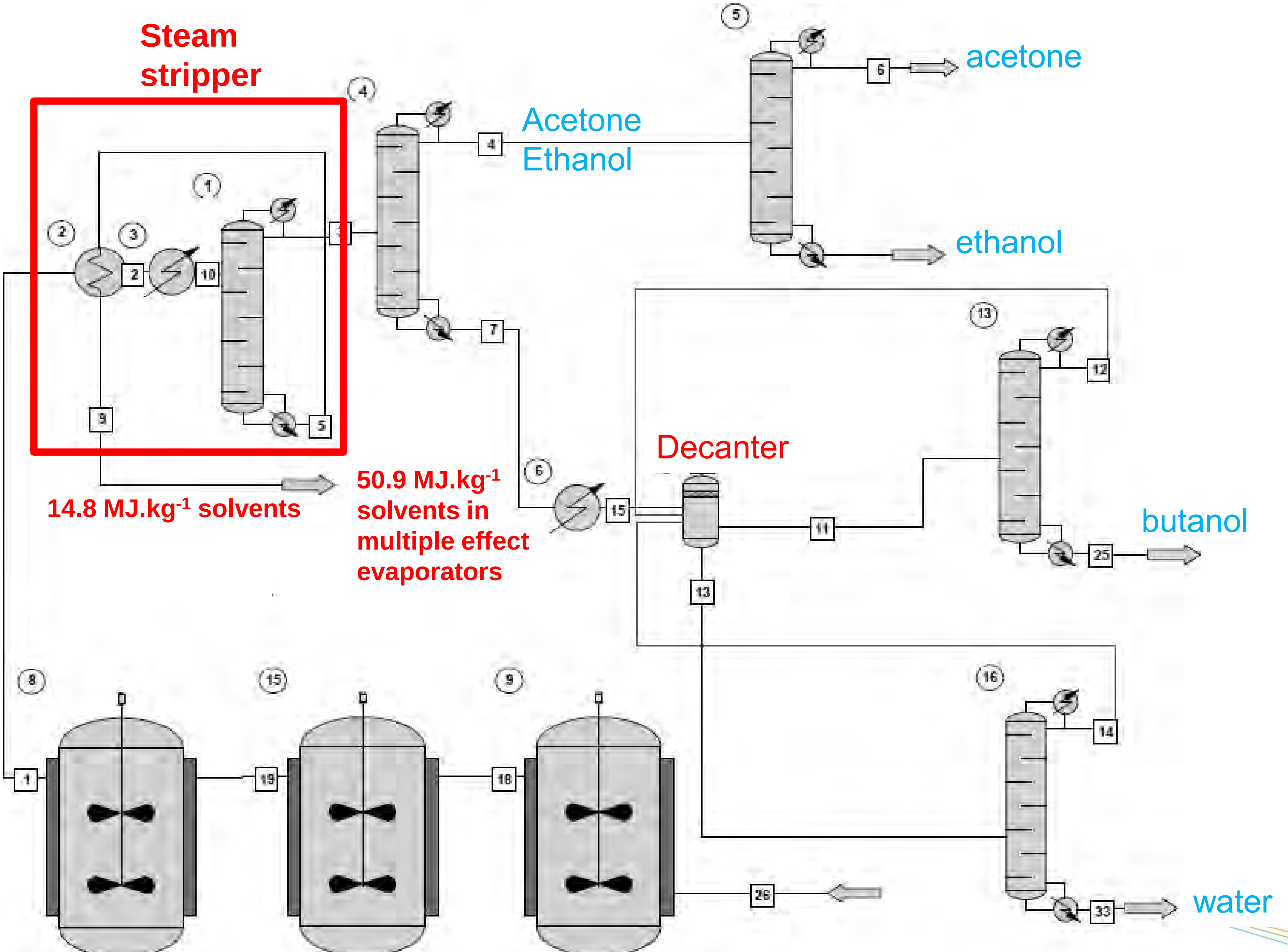
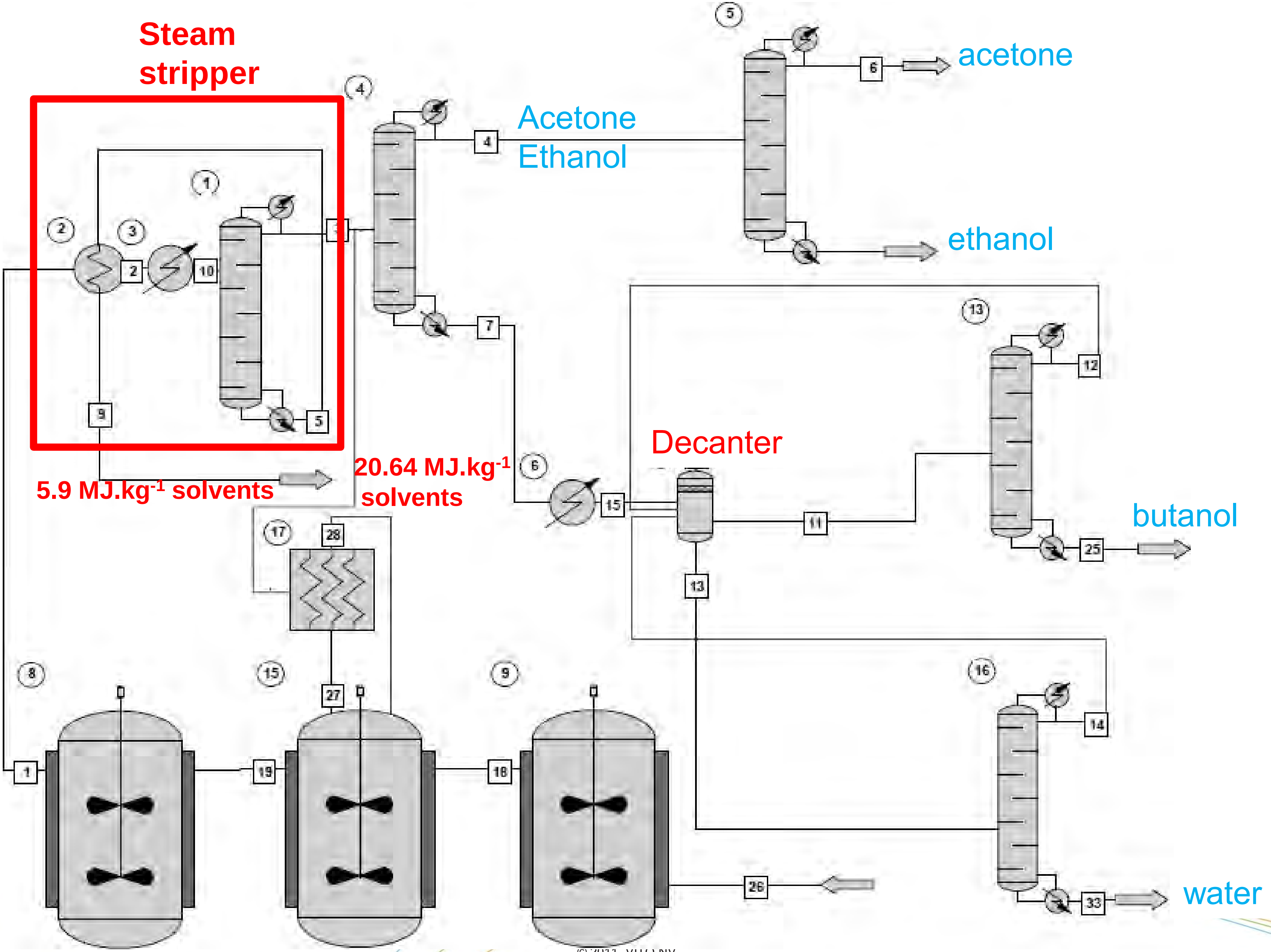
Introduction: PV for *in situ* recovery of solvents



Continuous conversion in a two-stage fermentation using a commercial composite membrane with PDMS top layer




Steam stripper
Acetone
Ethanol
acetone
ethanol
Decanter
butanol
water
14.8 MJ.kg-1 solvents
50.9 MJ.kg-1 solvents in multiple effect evaporators



Steam
stripper
Acetone
Ethanol
acetone
ethanol
Decanter
butanol
water
5.9 MJ.kg-1 solvents
20.64 MJ.kg-1
solvents

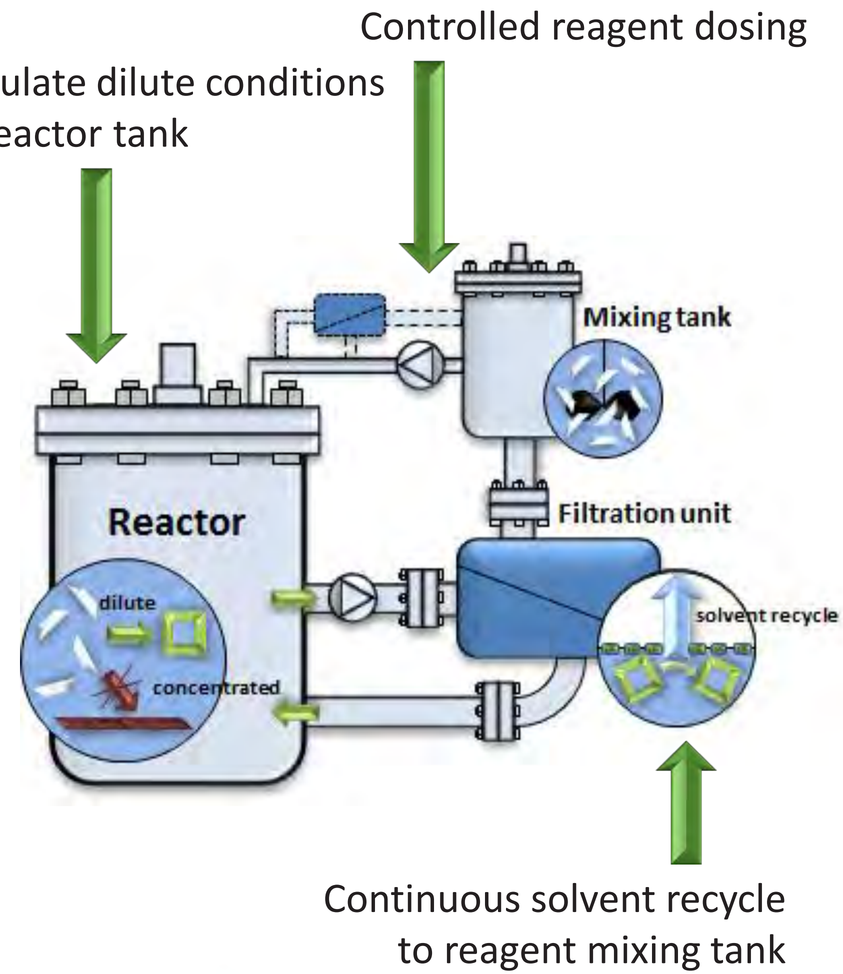
Volume Intensified Dilution

Concentration-sensitive reactions

- Require large solvent and reactor volumes
- Small amount of product is obtained
- Many pharmaceutical reactions
- i.e. macrocyclisation reactions: in concentrated media side-reactions result in unwanted (oligo-) polymerized product

Also applicable for:

- Reactions limited by substrate inhibition and precipitation
- Not only OSN filtration applications



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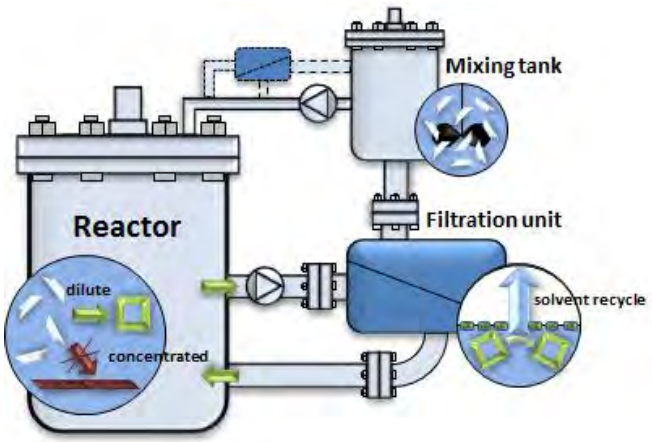
Volume Intensified Dilution



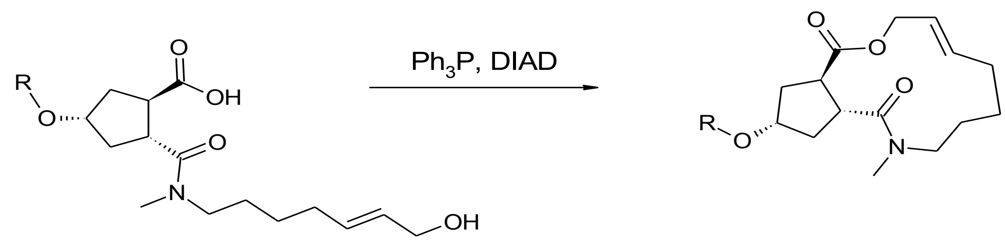
Lab-scale demonstration @VITO

- Both ceramic and polymeric OSN membranes used
- Reaction performances compared to state-of-the-art batch operation, performed at same reaction concentrations and conditions.

Similar yields + Process Mass Intensity (PMI) reductions of more than 40 % in a non-fully optimized system

Currently other reactions are being evaluated at VITO, where a PMI decrease of even 85 % has been achieved.

Mitsunobu reaction to form a 13-membered ring, in dichloromethane (DCM) and tetrahydrofuran (THF)



Chemical Formula: $C_{32}H_{41}N_3O_6S$
Molecular Weight: 595.75

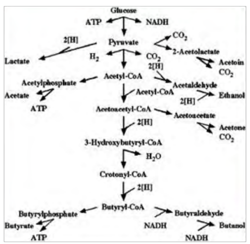
Chemical Formula: $C_{32}H_{39}N_3O_5S$
Molecular Weight: 577.73

Challenges

Feedstocks

- *Agricultural waste: straw, corn stover*
- *Industrial waste: sawdust, paper pulp*

Metabolic engineering



- Strain engineering
- Enzymes
- Catalysts

Process development

- *Continuous fermentation*
- *Cell retention*
- *ISPR*

Down-stream processing

- *Pervaporation*
- *Liquid-liquid extraction*
- *...*

Molecules:

- Drop ins
- Innovative molecules

⇩

Innovative Polymers/materials

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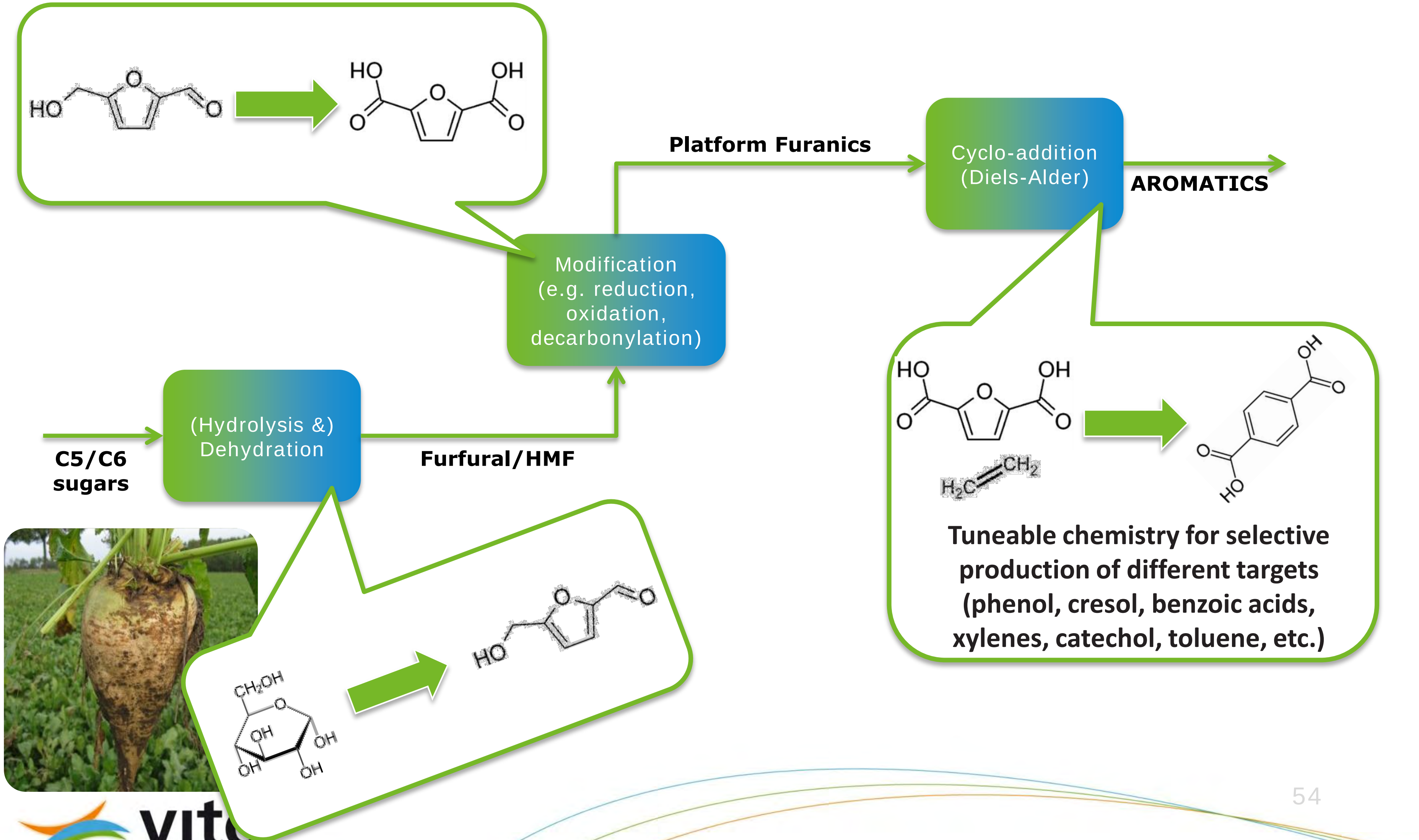
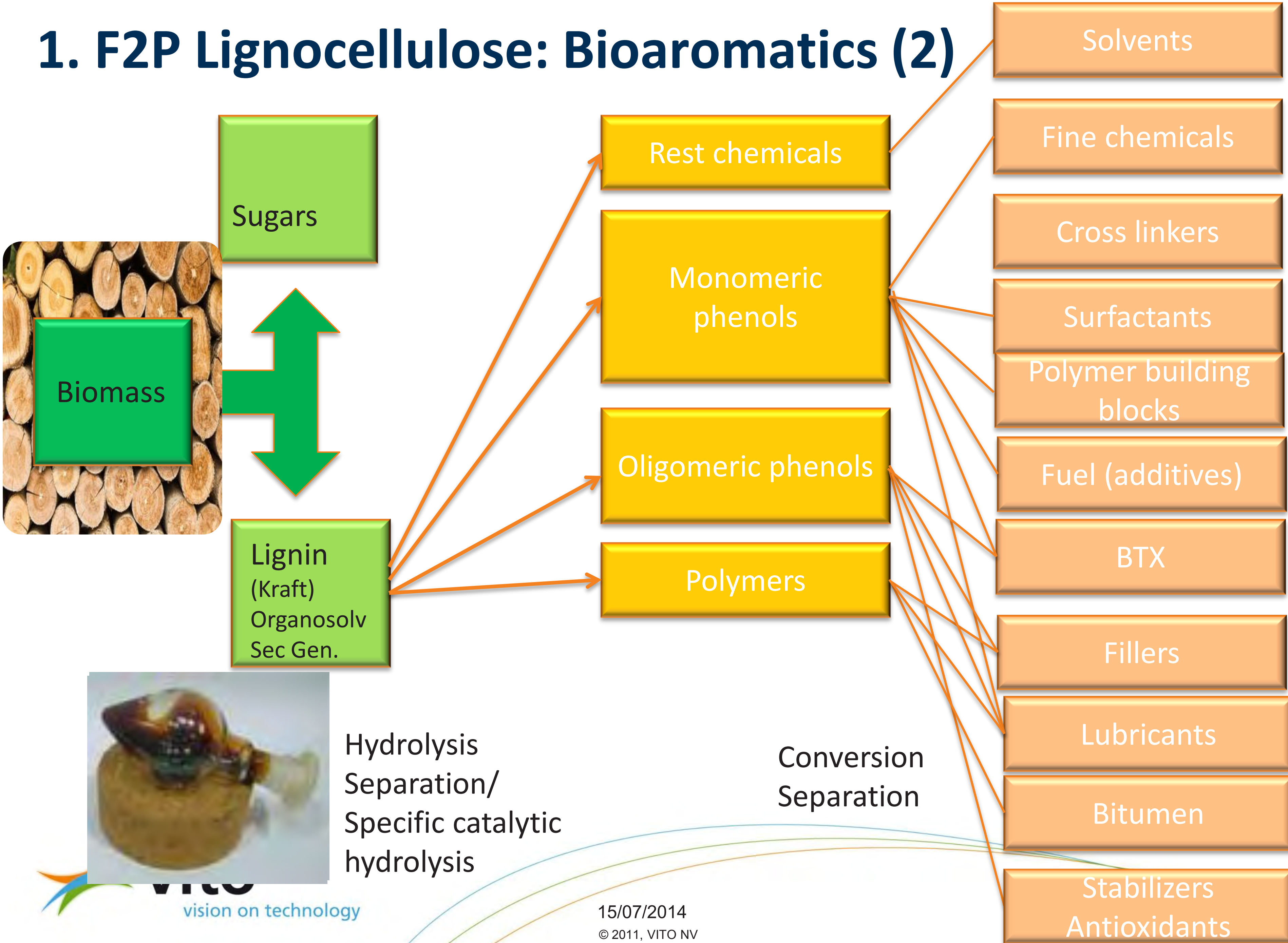
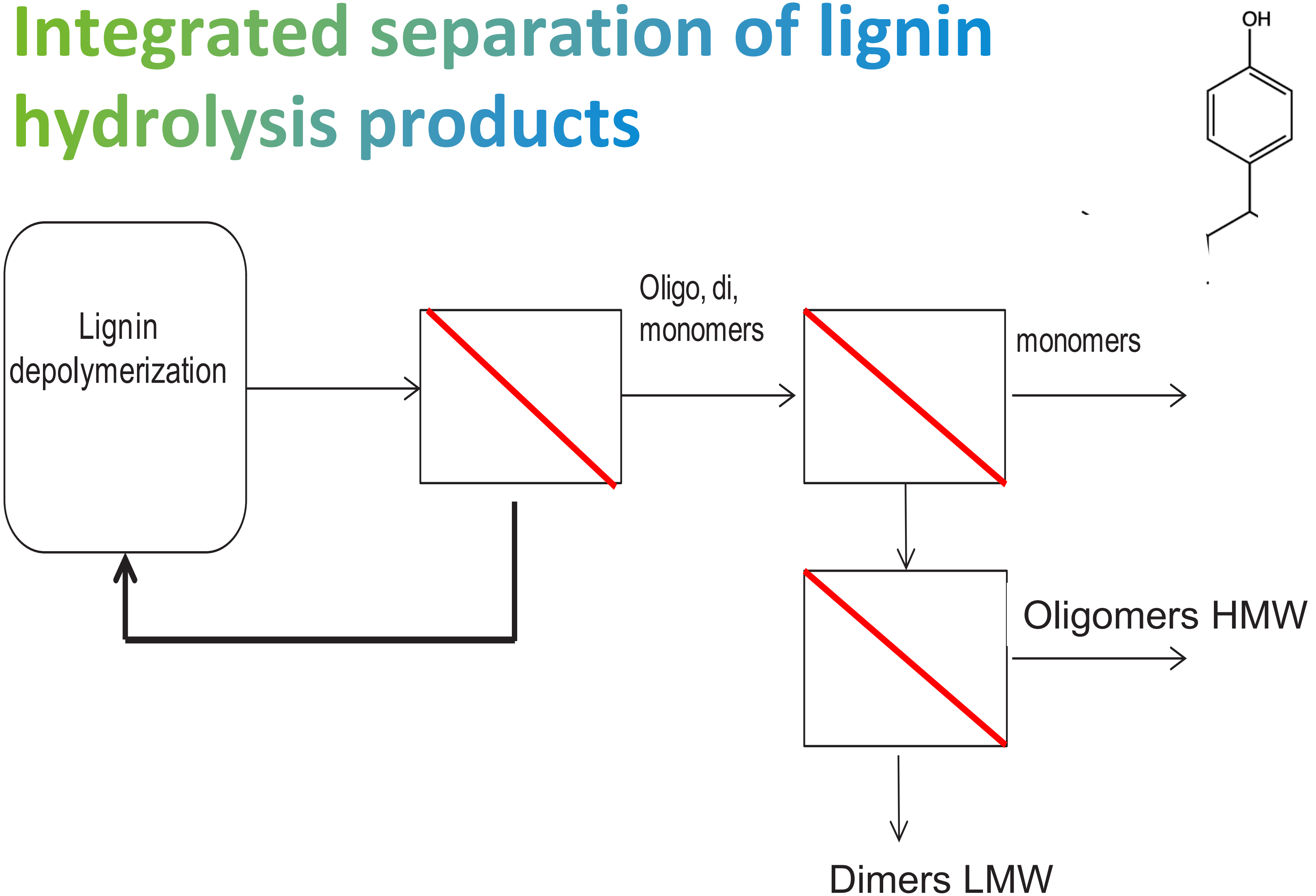
1. F2P Lignocellulose: Bioaromatics (1)



1. F2P Lignocellulose: Bioaromatics (2)



Integrated separation of lignin hydrolysis products



Outline

» Flanders driven by Chemistry

» Smart specialisation (New feedstock, Process Intensificiation)

» International Initiatives of Clustering and Smart Specialisation

» Conclusions

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Conclusions

- Chemical megacluster in a smart specialisation to renewables
  - Bio-based feedstock (including residues)
  - CO2
- Bio-based processes must be intensified as petroleum-based
  - From batch to continuous process (flow technology)
  - ISPR (reduce dilution, toxicity, dsp costs, etc.)
  - Combine with catalysis
  - Combine with (bio)electrochemical processes
- International collaboration, clustering and smart specialisation
  - FISCH
  - BIORIZON, the way to aromatics
  - BIG-C:
  - Link with other inititives (Greenwin-Valbiom, IAR, Rhône-Alpes, Danube cluster, …)

Thanks!
Questions?

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i-SUP2014, Antwerp, 1-3 September
www.i-sup2014.org