Società Chimica Italiana
Divisione di Didattica Chimica

Accademia Nazionale delle Scienze detta dei XL 1782

Piano Nazionale Lauree Scientifiche

VII SCUOLA NAZIONALE DI DIDATTICA DELLA CHIMICA "GIUSEPPE DEL RE"

La Chimica per uno sviluppo sostenibile e l'educazione civica

Bertinoro (FC), 6 - 9 ottobre 2022

Bioraffineria

Bertinoro, 8 ottobre 2022

Teresa Cecchi

ITT Montani, Fermo FM

teresacecchi@tiscali.it

*Three pillars of the multifaceted sustainability concept

The triple bottom line: planet, people, profit

- **Decoupling of production from fossil feedstock**
- **Breakthrough of renewable resources**
- **Zero waste approach**

https://link.springer.com/book/10.1007/978-3-030-63436-0

European Commission

What is the European Green Deal?

December 2019
#EUGreenDeal

The European Green Deal is about **improving the well-being of people**. Making Europe climate-neutral and protecting our natural habitat will be good for people, planet and economy. No one will be left behind.

The EU will:

- Become climate-neutral by 2050
- Protect human life, animals and plants, by cutting pollution
- Help companies become world leaders in clean products and technologies
- Help ensure a just and inclusive transition

TRANSFORMING THE EU'S ECONOMY FOR A SUSTAINABLE FUTURE

https://ec.europa.eu/info/sites/info/files/european-green-deal-communication_en.pdf

CLIMATE

The EU will be **climate neutral in 2050**.
The Commission will propose a European Climate Law turning the political commitment into a legal obligation and a trigger for investment.

Reaching this target will require action by all sectors of our economy:

ENERGY

Decarbonise the energy sector

The production and use of energy account for more than **75%** of the EU's greenhouse gas emissions

BUILDINGS

Renovate buildings, to help people cut their energy bills and energy use

40% of our energy consumption is by buildings

INDUSTRY

Support industry to innovate and to become global leaders in the green economy

European industry only uses **12%** recycled materials

MOBILITY

Roll out cleaner, cheaper and healthier forms of private and public transport

Transport represents **25%** of our emissions

2050: Climate and Carbon neutral Europe

https://ec.europa.eu/clima/policies/strategies/2050_en
net-zero greenhouse gas emissions

Bio-Based vs fossil-based chemicals

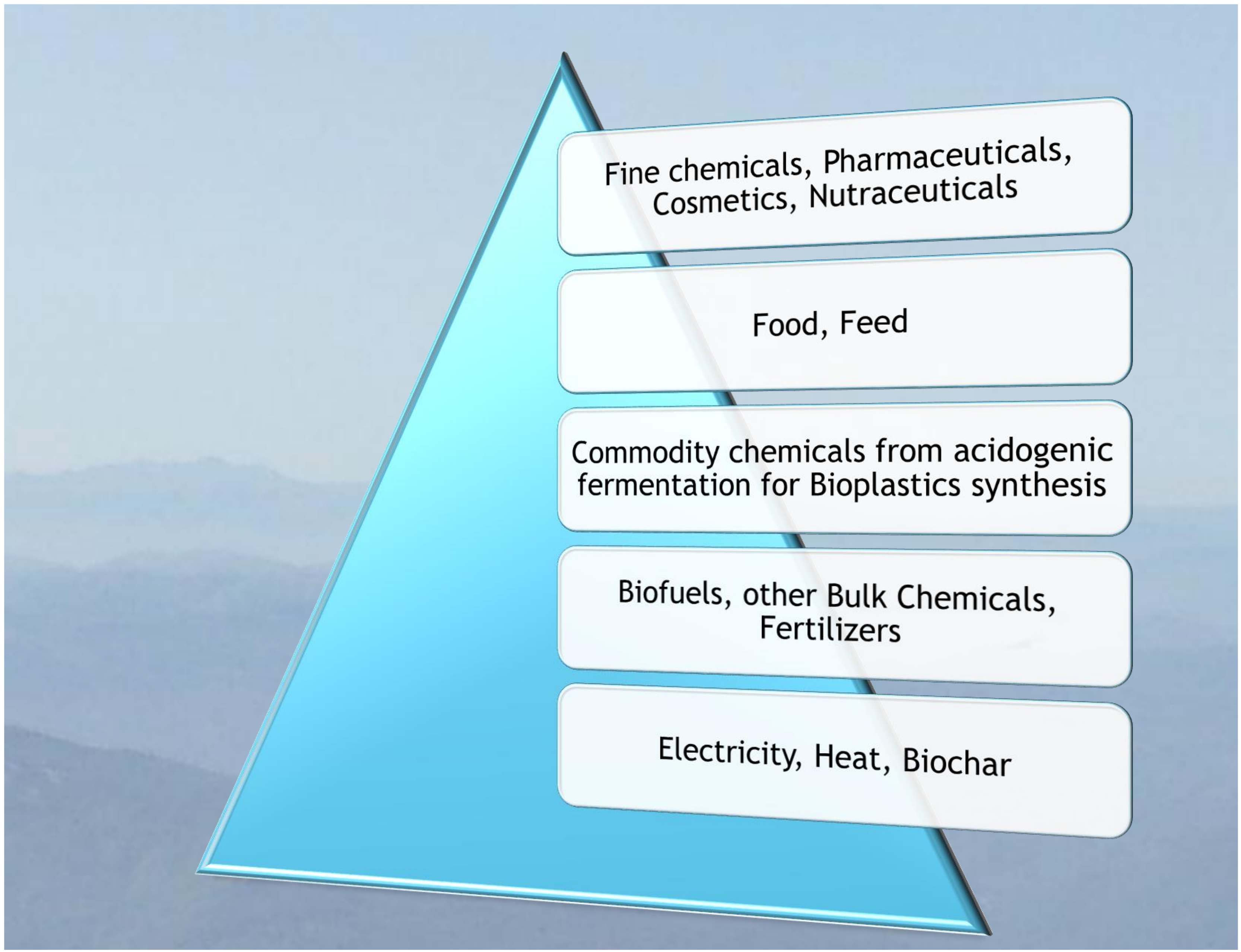
https://ec.europa.eu/energy/sites/ener/files/documents/EC%20Sugar%20Platform%20final%20report.pdf
https://op.europa.eu/en/publication-detail/-/publication/8eccea76-1ec7-11e9-8d04-01aa75ed71a1/language-en/format-PDF/source-114884626

1. **Decoupling of production of chemicals, materials and fuels from fossil feedstock taking building block from renewable resources**
2. **Consumables are returned to the biosphere without negative effects after a sequence of bio-cascading steps in a climate and carbon neutral world**
3. **Renewable energy is used to fuel the processes**
4. **Zero waste approach (waste does not exist because atoms are not destroyed in chemical reactions): recycling and upcycling**
5. **Focus on non-renewable resources**

Directive 2008/98/EC, WASTE Hierarchy

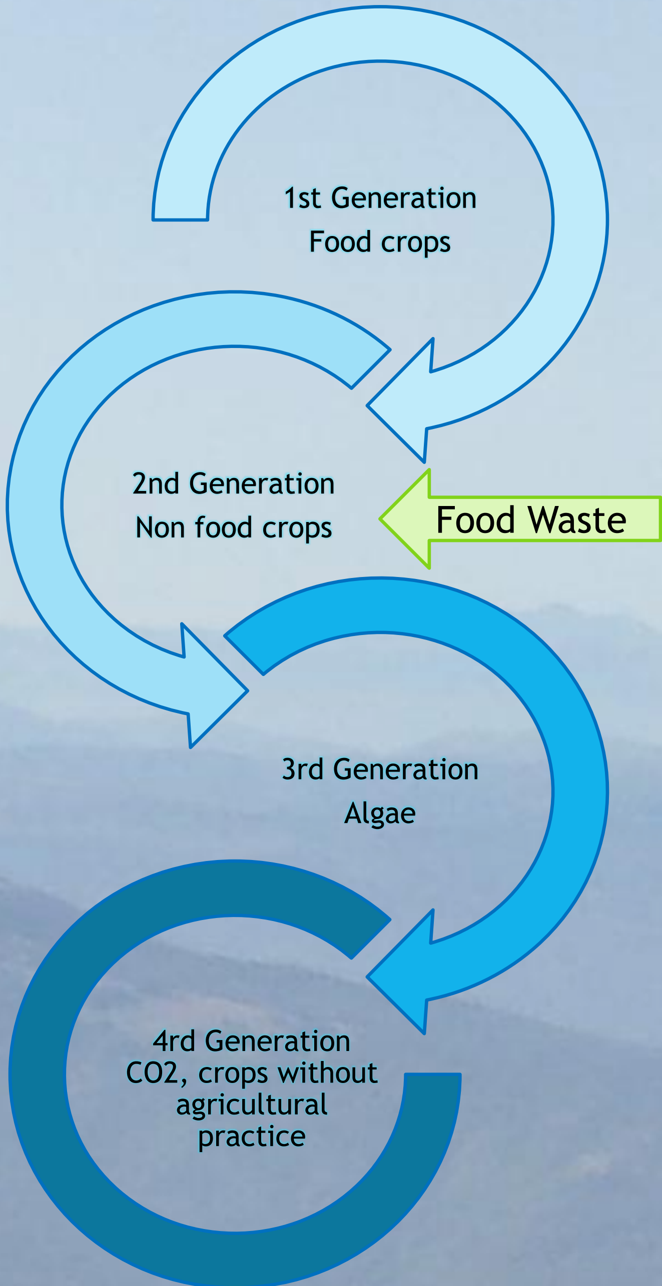
https://link.springer.com/book/10.1007/978-3-030-63436-0

Cascading Pyramid approach: biomass is used sequentially as effectively possible, first as material and finally for energy.

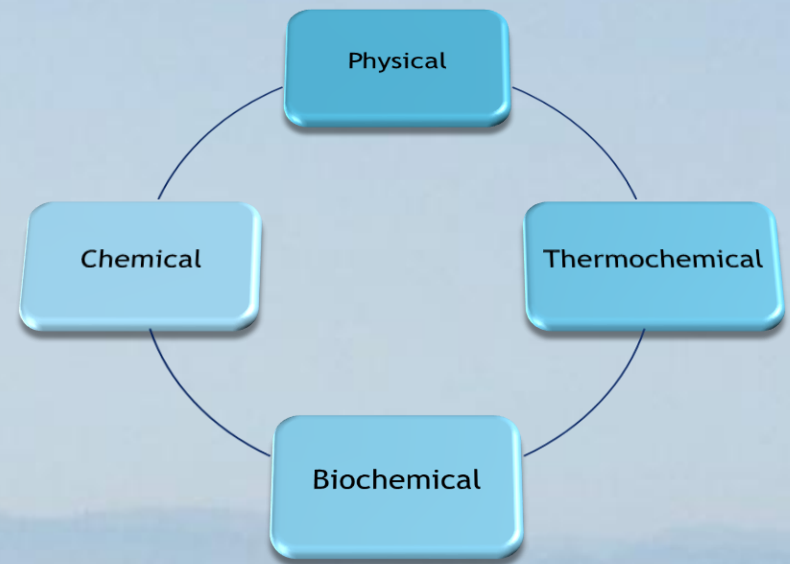


https://link.springer.com/book/10.1007/978-3-030-63436-0

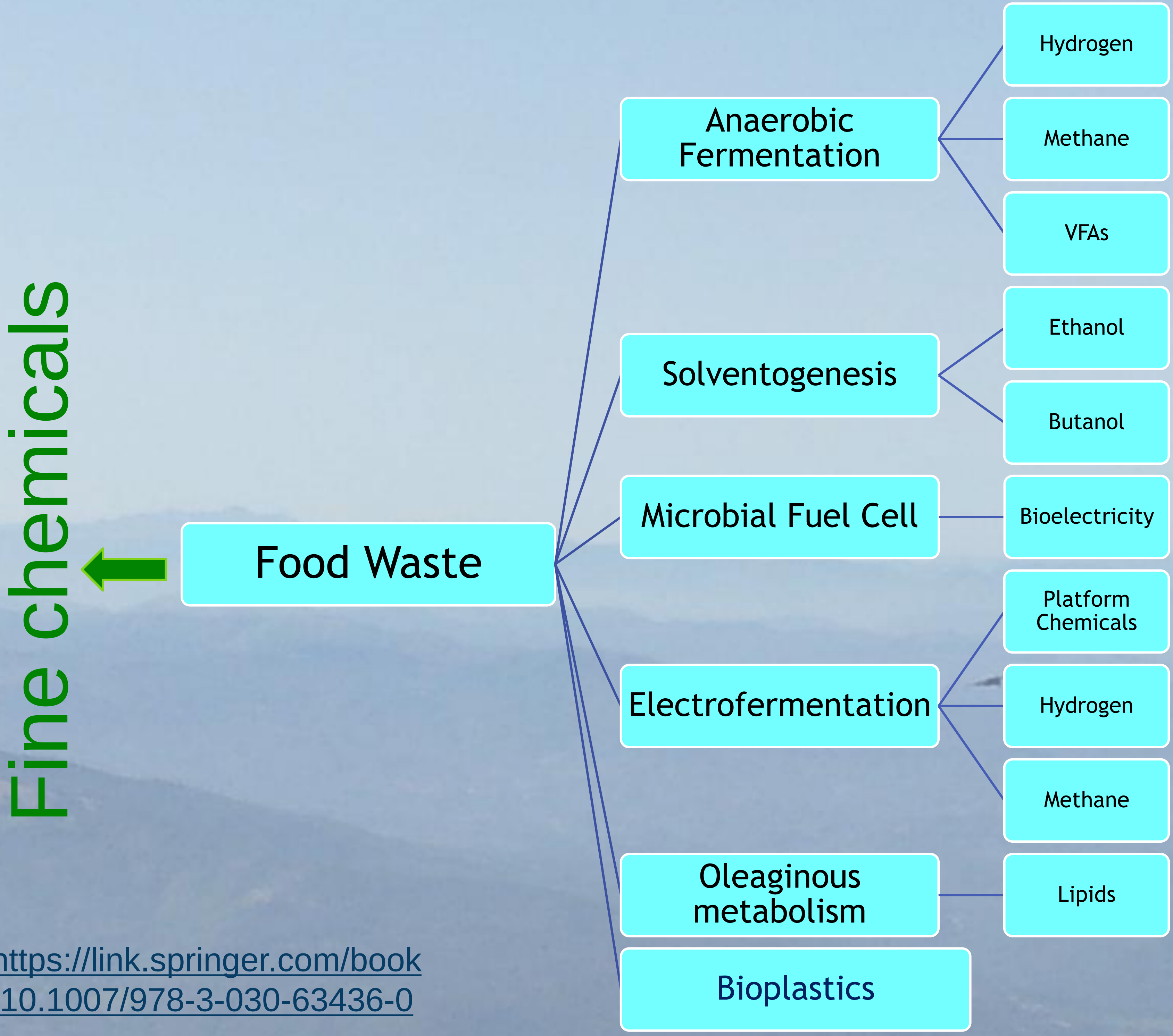
Raw Material Selection



Transformation Technology Selection



https://link.springer.com/book/10.1007/978-3-030-63436-0



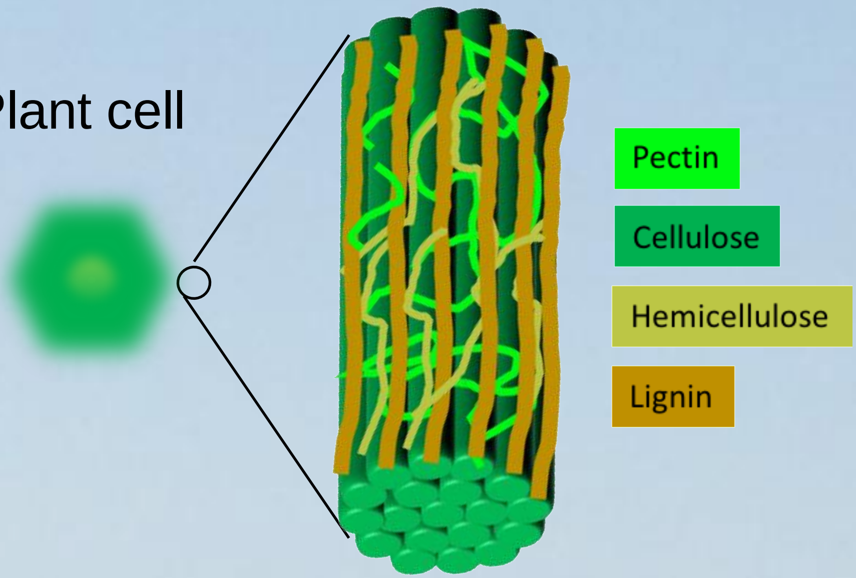
https://link.springer.com/book/10.1007/978-3-030-63436-0

*PPW

- 370 million tons worldwide
- PPW is 15–40% of the initial potato weight
- Landfilling is the current PPW management strategy
- Challenges:
  - Polymeric carbohydrates (starch and lignocelluloses) must be hydrolysed to fermentable sugars to be utilized by microorganisms
  - Glycoalkaloids have inhibitory effects on several bacteria

https://link.springer.com/book/10.1007/978-3-030-63436-0
Muhondwa, et al.2015. Int. J. Environ. Res. 9 (2), 481.
Barampouti et al., 2021. https://doi.org/10.1007/s13399-021-01811-4

Plant cell

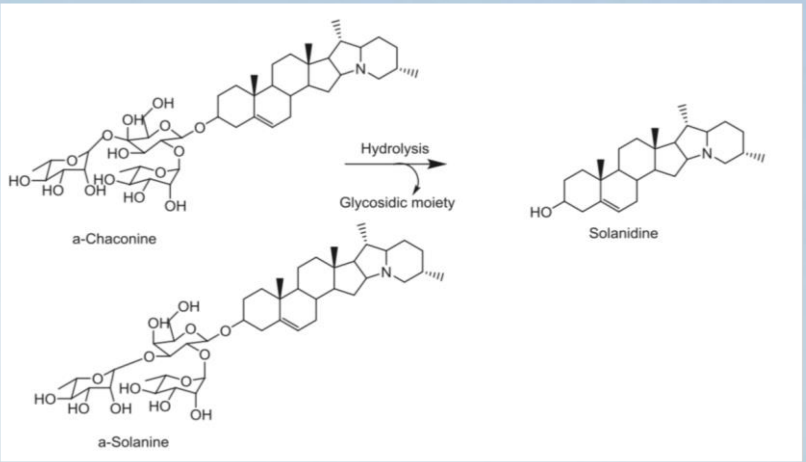


Microfibril in the cell wall

Resins and flavour compounds

Sugars → Biofuels, Biochemicals, Bioplastics

Starch
16-35%



PPW

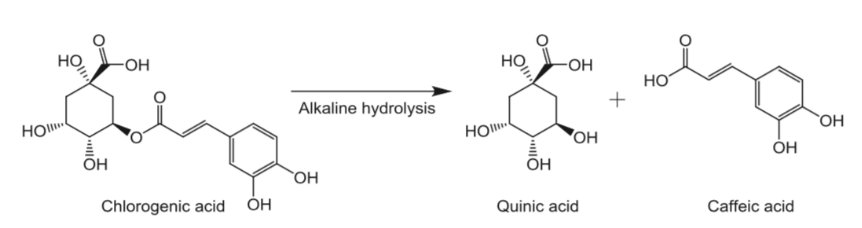
Lignocelluloses, 44-65%

Proteins

Lipids

Glycoalkaloids (α-chaconine, α-solanine) 0.6–3.6 mg/g dry PPW

- inhibitory efects on bacteria
- anticancer, anti-inflammatory, and anti-obesity effects
- precursors in the manufacturing of antibiotics and hormones



Phenolic compounds: antioxidants and antimicrobial
Quinic acid (starting material for Oseltamivir)
Caffeic acids (antimicrobial)

https://link.springer.com/book/10.1007/978-3-030-63436-0

PPW Cascading Pyramid

- multiple bioproducts
- waste minimization

1-Physical pretreatment

2-Extraction
GRAS solvents

Glycoalkaloids, Phenolics

3a-Pretreatment to destruct lignin
Chemical: H^+, OH^-, safe sovents
Biochemical, not efficient
Thermochemical, energy demanding (high T extrusion, steam explosion)
Emerging technologies (IL, DES, SFE)

Inhibitors (5-HMF, furfural, phenolics) from degradation of hemicellulose and lignin

4a-Hydrolysis
Acidic or enzymatic(!) (hemicellulase, cellulase, amylases)

EtOH and Solventogenesis (ABE)
H_2(dark ferm., H_2 producing bacteria)
Biopolymes (PHA)
Biochemicals (xanthan, enzymes)
Biogas

5a-Fermentation

3b/6a-Thermochemical processing
Pyrolysis and Hydrothermal liquefaction

Bio-oil, Biochar (biosorbent)

12 Principles - Green Chemistry

https://royalsocietypublishing.org/doi/pdf/10.1098/rsos.191378

Basic concepts of extraction

* Analyte distribution between two immiscible phases
* K=f(T, phases nature, analyte nature)
* Tradeoff between selectivity and extraction efficiency
* Reduced thermal decomposition of thermos-labile components
* Green chemistry:
  * GRAS solvents
  * shorter extraction time,
  * energy efficiency
  * Efficient solvent removal from the extracts

Estrazione di acidi fenolici e glicoalcaloidi

MATERIALI

- Patate
- Blender domestico
- Bagno ad ultrasuoni
- Beker adatto al mixer
- Beker da 50 ml per la raccolta del filtrato
- Cilindri da 100 e 10 ml
- 100 ml di miscela d' estrazione con 46% acqua, 51% etanolo, 3% acido acetico
- Imbuto e carta da filtro
- Bacchetta di vetro
- guanti
- parafilm

METODO

- 5 grammi buccia patata
- 12.5 ml del solvente di estrazione
- Omogeneizzare la miscela con mixer in un beker adatto
- Lasciare la miscela 30 min al buio
- Ultrasuoni per 20 min
- Filtrazione, raccolta del filtrato in beker da 50 ml
- Test del potere antiossidante con miscela BR del filtrato
- Eventuale SPE C18 del filtrato: eluizione di acidi fenolici (80%H_2O 20% EtOH) e glicoalcaloidi (20%H_2O 80% EtOH)

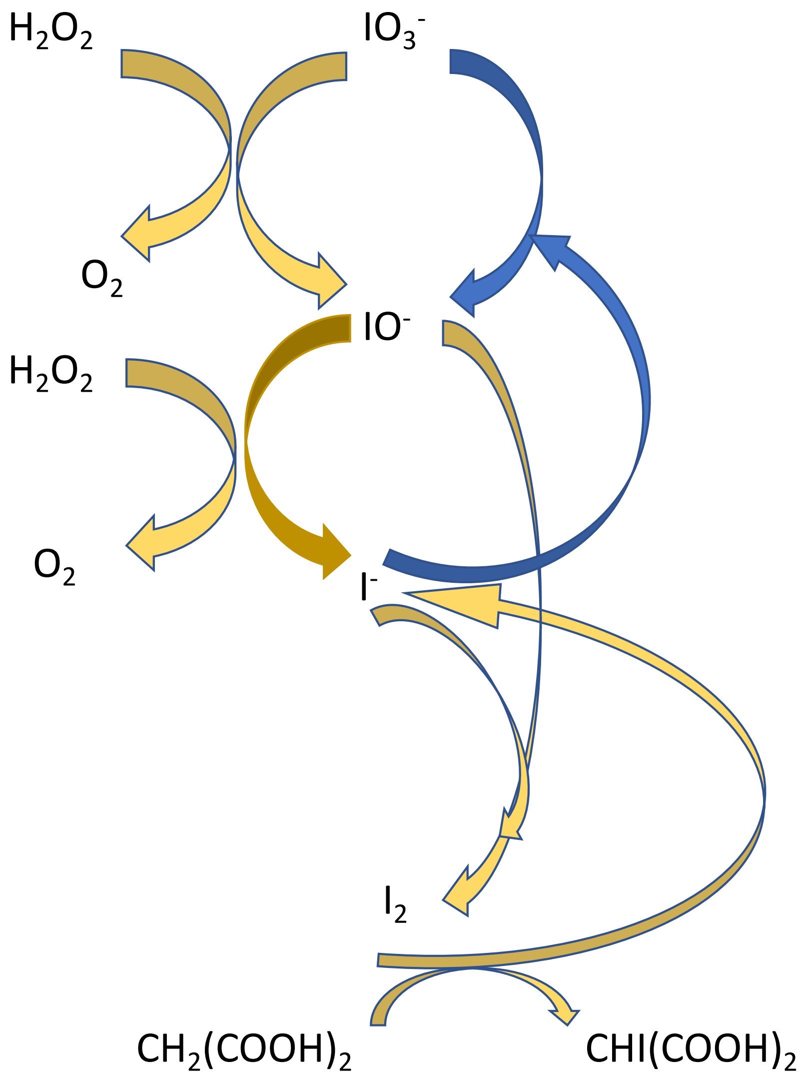


Fig. 1. Explanation of the chemistry involved in the BR reaction:

$IO_3^- + 2\ H_2O_2 + CH_2(COOH)_2 + H^+ \rightarrow ICH(COOH)_2 + 2\ O_2 + 3\ H_2O$ (1)

The BR reaction is accomplished through two component reactions:

$IO_3^- + 2\ H_2O_2 + H^+ \rightarrow HIO + 2\ O_2 + 2\ H_2O$ (2)

$HIO + CH_2(COOH)_2 \rightarrow ICH(COOH)_2 + H_2O$ (3)

Eq.(2) can follow both a fast radical path, involving the HOO· and the redox chemistry of the catalyst (Mn^{++}), or a non radical path when the $[I^-]$ is low and high, respectively.

Eq. (3) is a two step reaction

$I^- + HIO + H^+ \rightarrow I_2 + H_2O$ (4)

$I_2 + CH_2(COOH)_2 \rightarrow ICH(COOH)_2 + H^+ + I^-$ (5)

Upon initial mixing of the solutions, IO_3^- reacts with H_2O_2 to produce, via a **fast radical** path, a rapidly increasing $[IO^-]$. IO^- is partly reduced to I^- by H_2O_2 and partly reacts with I^-, producing I_2 according to Eq (4) (AMBER SOLUTION, RADICAL PATH). I_2 reacts slowly with malonic acid, thereby causing an increase in $[I^-]$ according to Eq. (5). Its high concentration triggers its reaction with IO_3^- and hence a **slow non radical** production of IO^- (BLUE SOLUTION NON RADICAL PATH). IO^- and I^- are consumed in the idodination of malonic acid at a faster rate compared to that of their slow production. Eventually $[I^-]$ is reduced to such a low value that the radical process takes over again. This oscillating sequence repeats until the malonic acid or IO_3^- is depleted.

*Briggs Rausher reaction

* A: 5ml H2O2 conc 5 ml H2O
* B: 10 ml di una soluzione 0.2M in NaIO3 e 0.1M in HClO4
* C: 10 ml di una soluzione contenente 0.15M ac malonico e 0.02M in MnSO4 monoaidrato

* Unire in sequenza la sz B, sz C, 4 gocce di salda d'amido e infine la sz A

Soluzioni per la reazione di Briggs Rauscher

Other possibilities

Tipo di residuo	Prodotto	Consumo materie prime	Processi e Condizioni Operative	Autore
Scarti di patate 5g	Acido Lattico	3g $CaCO_3$, L. cellobiosus, 100ml H_2O	37°C per 48 ore, far bollire e schiacciare, agitare a 300 giri/min	Chatterjee et al. 1997
Purè di patate di scarto	Alfa-amilasi	L. cellobiosus	24h	Chatterjee et al. 1997
16,16 g peso secco di Purè di scarto di patate	Etanolo	4mg alfa-amilasi, 6.19L acqua, 3.2 ml amiloglucosidasi, Inoculo al 3% N (da pollame)	Liquefazione: ph6.5, 3h a 95° a 120giri/min. saccarificazione: 72, 120giri/min, 60°C fermentazione: 30°, 48h, ph5.5	Izmirlioglu et al. 2012
Massa di patate di scarto	65.8g/L bioetanolo	S. Cerevisiae 19.2g/L, HCL al 2.1%	Idrolisi HLC Ultrasuoni a 340W, 7min	Suresh et al 2020
Bucce di patate	Acidi fenolici HMF Biochar	H_2SO_4, LiBr, $AlCl_3$, Solvente 2-butanolo	Essiccato sottovuoto a 50°C, malta ceramica, estrazione ad ultrasuoni per 15 min, filtrazione, centrifugazione 10 min 5°C	Ebikade et al 2020
Scarti di patate dolci	Etanolo	Energia Elettrica 128.3 kWh, Acqua 29.58m3 Enzima per idrolisi [L/kg SWP] 0.001, Enzima per riduzione viscosità 0.0001, Lievito [kg/kg SWP] 0.0033, Antibiotico tetraciclina 0.0003, Legna da ardere 2.2m^3	Pulito, tagliato a cubetti, cotto a vapore fino a 76°C, raffreddato, frantumato, coltivato in shaker orbitale a 34°C per 19h, distillazione finale	Weber et al. 2020
Scarti di patate dolci	Igienizzante per le mani a base alcolica	Acqua, enzimi, lievito, legna vedi sopra, Energia elettrica [kWh] 140.02 agente addensante carbomer [kg/L igienizzante] 0.00245 Trietanolammina [L/L igienizzante] - 0.00004	Pulito, tagliato a cubetti, cotto a vapore fino a 76°C, raffreddato, frantumato, coltivato in shaker orbitale a 34°C per 19h, distillazione, mescolamento finale	Weber et al. 2020
Buccia di patate	Glucosio, resa al 49%	Sospensione acquosa di scarto di buccia 20% in peso, acqua 1gHsiW catalizzatore	Da amido a glucosio, irradiazione a microonde per 15 min; sottoprodotti: Acidi levulinico e formico	Kumar et al. 2016

Grazie per l’attenzione!

teresacecchi@tiscali.it