An introduction to circular chemistry

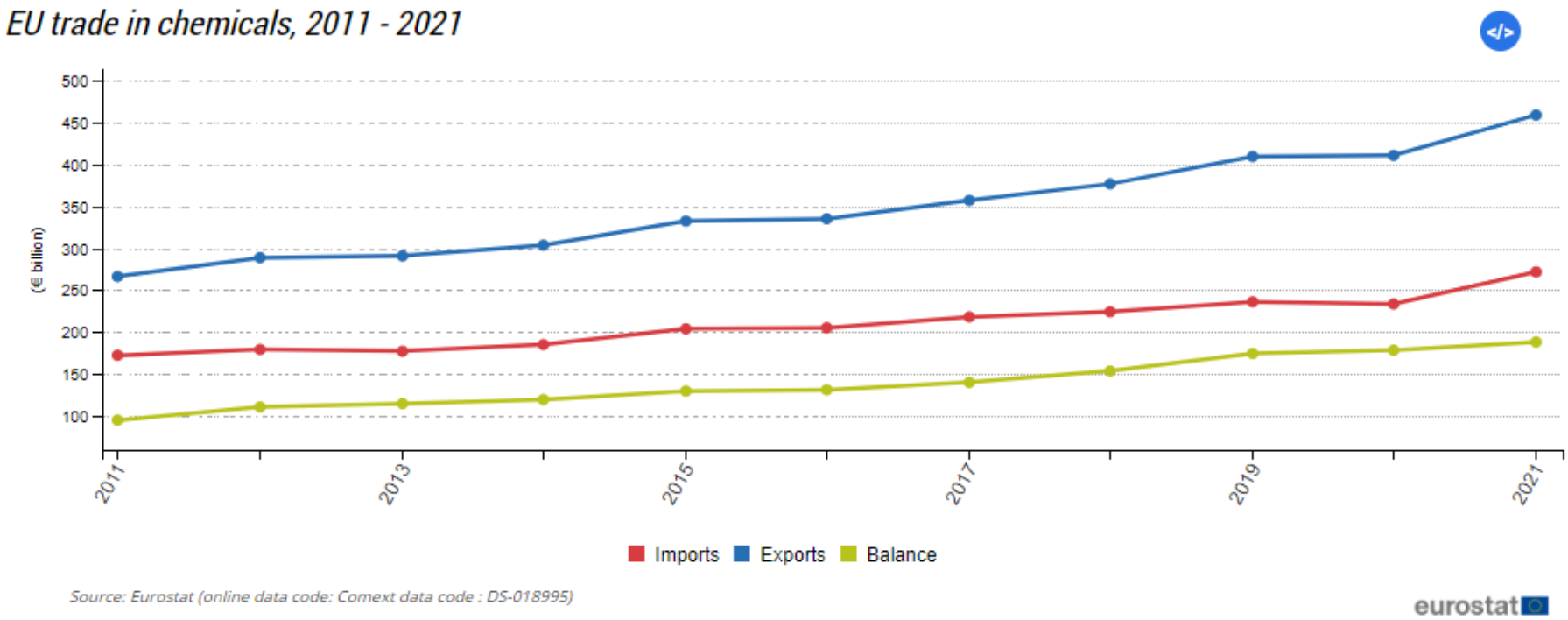


https://thenaturalstep.org/blog/2018/03/03/without-chemistry-there-can-be-no-circular-economy/

The starting points

- 140,000 industrial chemicals are marketed worldwide
- new chemicals are becoming more complex (e.g., stereochemistry, functional groups)
- most of today's chemical products are synthetic, based on nonrenewable resources, and formed into complex articles such as plastics.
- products of the chemical and related industries contain mixtures of elements and molecules, and these products and their constituents are found everywhere, including in waste products, soils, water, air, plants, food, animals, and the human body
- many materials need specific grades and mixtures of metals and other elements, and each of these demands separation and purification at the atomic and molecular levels in the recycling process
- recycling unavoidably leads to the downgrading of materials and dissipative losses of utilizable elements and energy
- the complexity and diversity of today's products and their components (on atomic, molecular, material, and building-block levels) enlarge this dissipation of metals and other elements, pollutants, and energy

The starting points



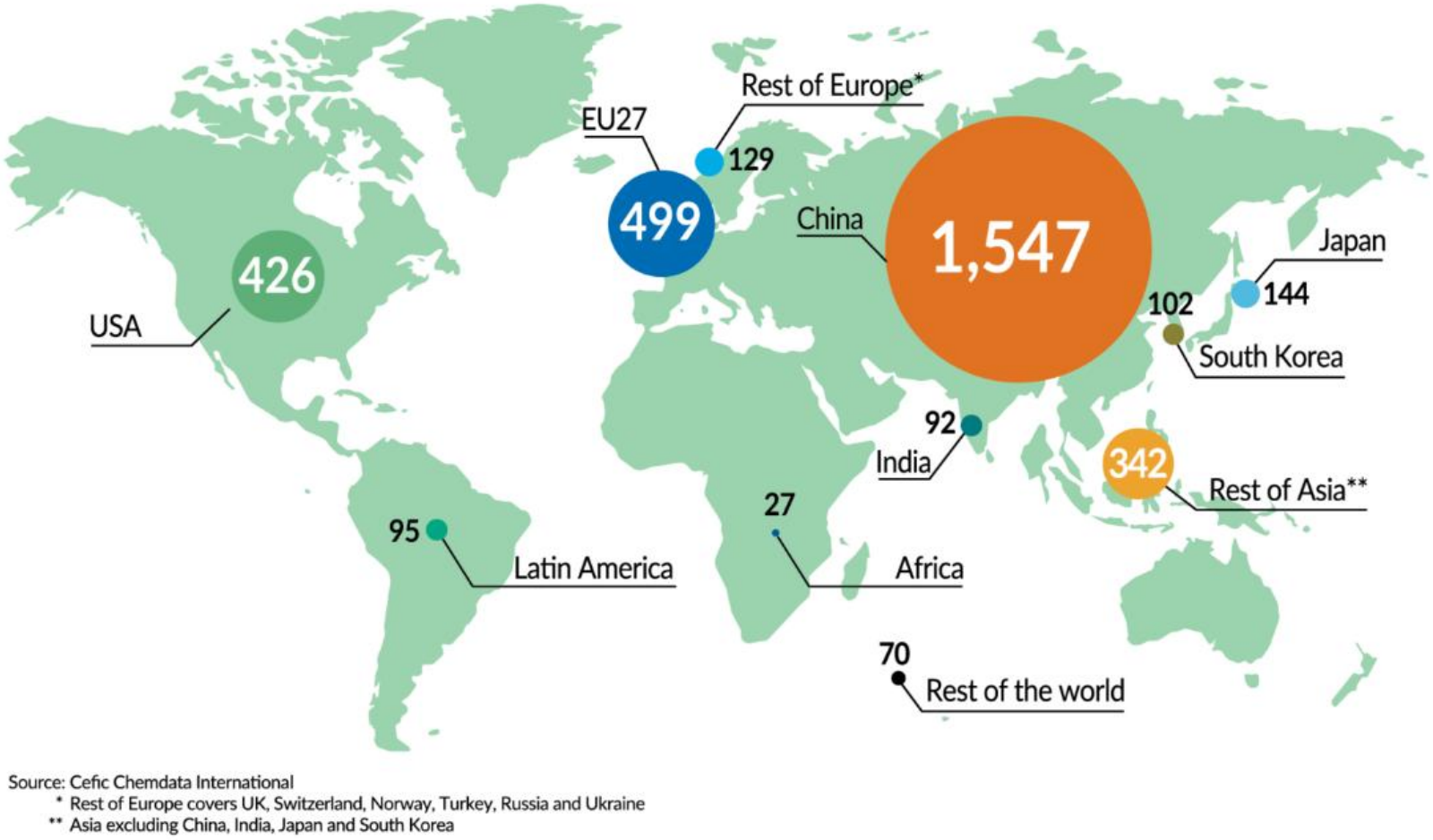
https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Production_and_international_trade_in_chemicals

The starting points

- World chemicals sales was valued at € 3,471 billion in 2020. Global sales decreased by 4.3% from € 3,628 billion in 2019 to € 3,471 billion in 2020.
- With 14.4%, the EU27 chemical industry ranks second in total sales, with the United States coming in third with 12.3%.
- Worldwide the competitive landscape has changed significantly over the last ten years. Today, next to the EU27, US and Japan mostly emerging countries from Asia rank in the top 10 in sales.

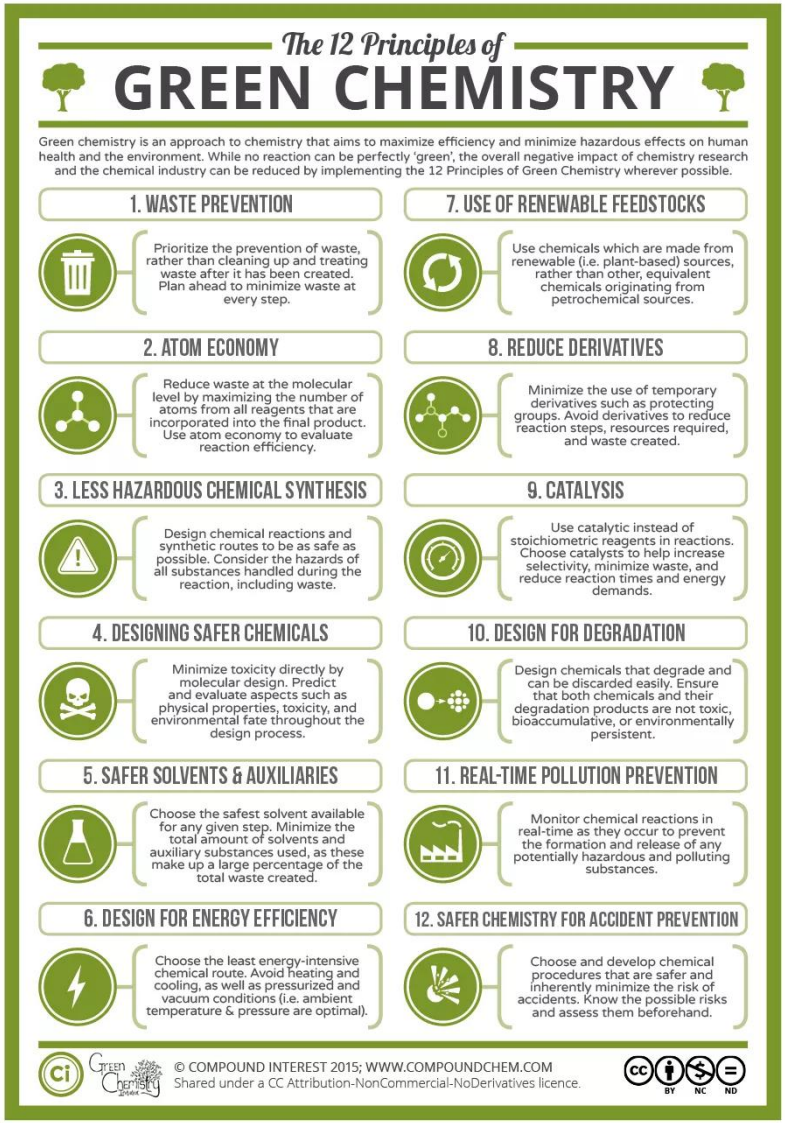
https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Production_and_international_trade_in_chemicals

The starting points



Source of figure: https://cefic.org/a-pillar-of-the-european-economy/facts-and-figures-of-the-european-chemical-industry/profile/

Why chemistry to support and nurture sustainable development





role of chemistry in understanding and protecting the environment

Why chemistry to support and nurture sustainable development

A Definition of Sustainable Chemistry

"Sustainable chemistry is a scientific concept that seeks to improve the efficiency with which natural resources are used to meet human needs for chemical products and services. Sustainable chemistry encompasses the design, manufacture and use of efficient, effective, safe and more environmentally benign chemical products and processes."

Sustainable chemistry is also a process that stimulates innovation across all sectors to design and discover new chemicals, production processes, and product stewardship practices that will provide increased performance and increased value while meeting the goals of protecting and enhancing human health and the environment.

Why chemistry to support and nurture sustainable development

- Understanding the composition and transformation of matter
- Understanding chemical processes occurring in the environment
- Understanding thermodynamics and its constraints
- Understanding the chemical fate of pollutants
- Design better and more efficient synthesis and production routes
- Design for recycling and loop closure
- Address materials criticality with more efficient design and/or substitution
- Design remediation and recycling approaches
- Nurture the three challenges in sustainable development:
  - Solar energy capture and conversion to electricity
  - Electric batteries to store energy
  - Better and more efficient biomass conversion of chemical to electric energy (also role of biotech to improved crops: presently only 1% of solar energy converted to chemical energy: role of *biotechnology*)

Why chemistry to support and nurture sustainable development

Examples of chemical **process** technology development include:

- Using alternative feedstocks that are more innocuous and renewable.
- Developing alternative synthetic pathways, such as the use of catalysis and biocatalysis, photochemistry, and biomimetic synthesis.
- Designing simpler reaction processes that reduce energy consumption and minimise the use and release of hazardous chemicals.
- Developing alternative reaction conditions for increased selectivity and waste reduction.

Examples of chemical **product** technology development include:

- Designing chemical products to minimise impacts on human health and the environment.
- Designing chemical products that have inherently less hazardous properties.
- Designing chemical products that have reduced toxicity, flammability, and explosion potential

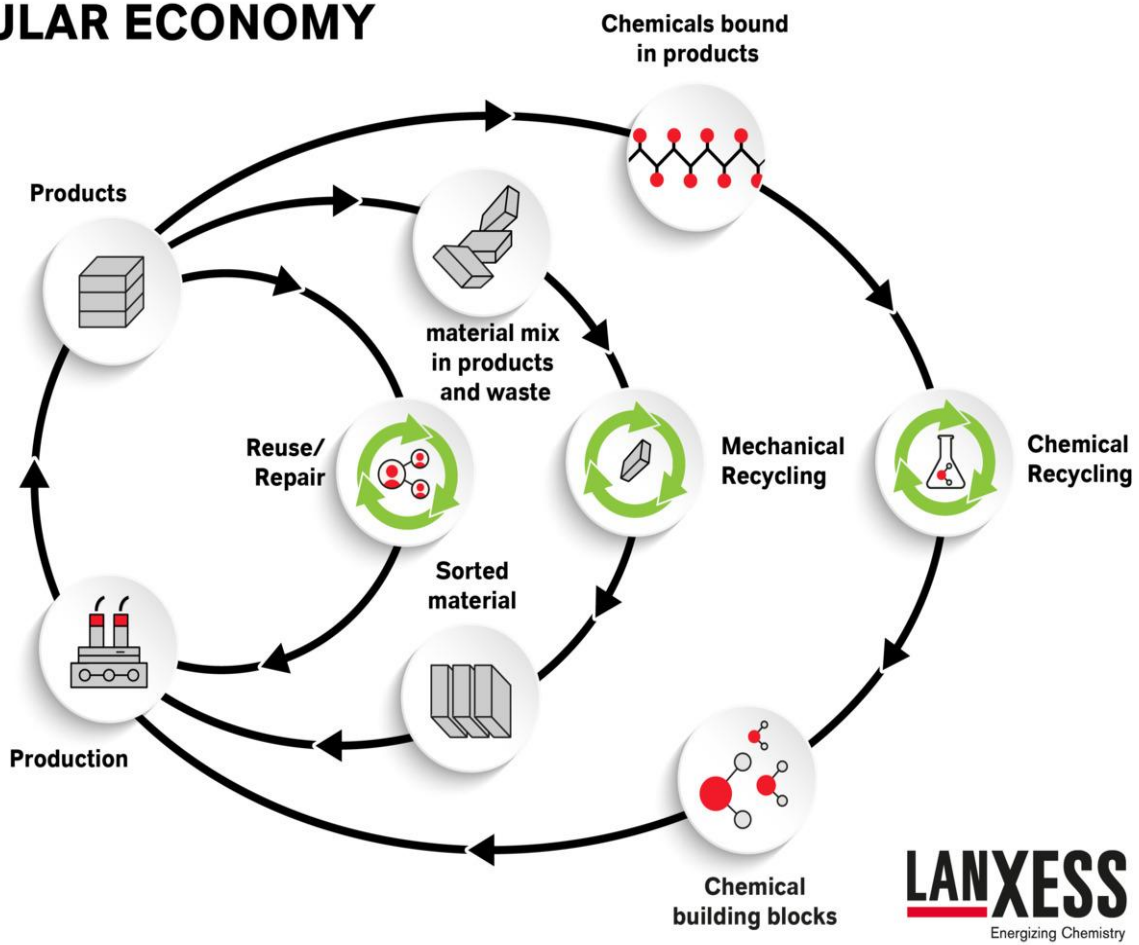
Circular Economy and the role of Chemistry

VALUE STREAMS IN A CIRCULAR ECONOMY

Reuse/Repair
Consumer goods or even chemicals can be leased and reused.

Mechanical Recycling
Decomposition without changing the chemical structure of the material includes collection, separation, grinding, melting, sorting, washing or filtering.

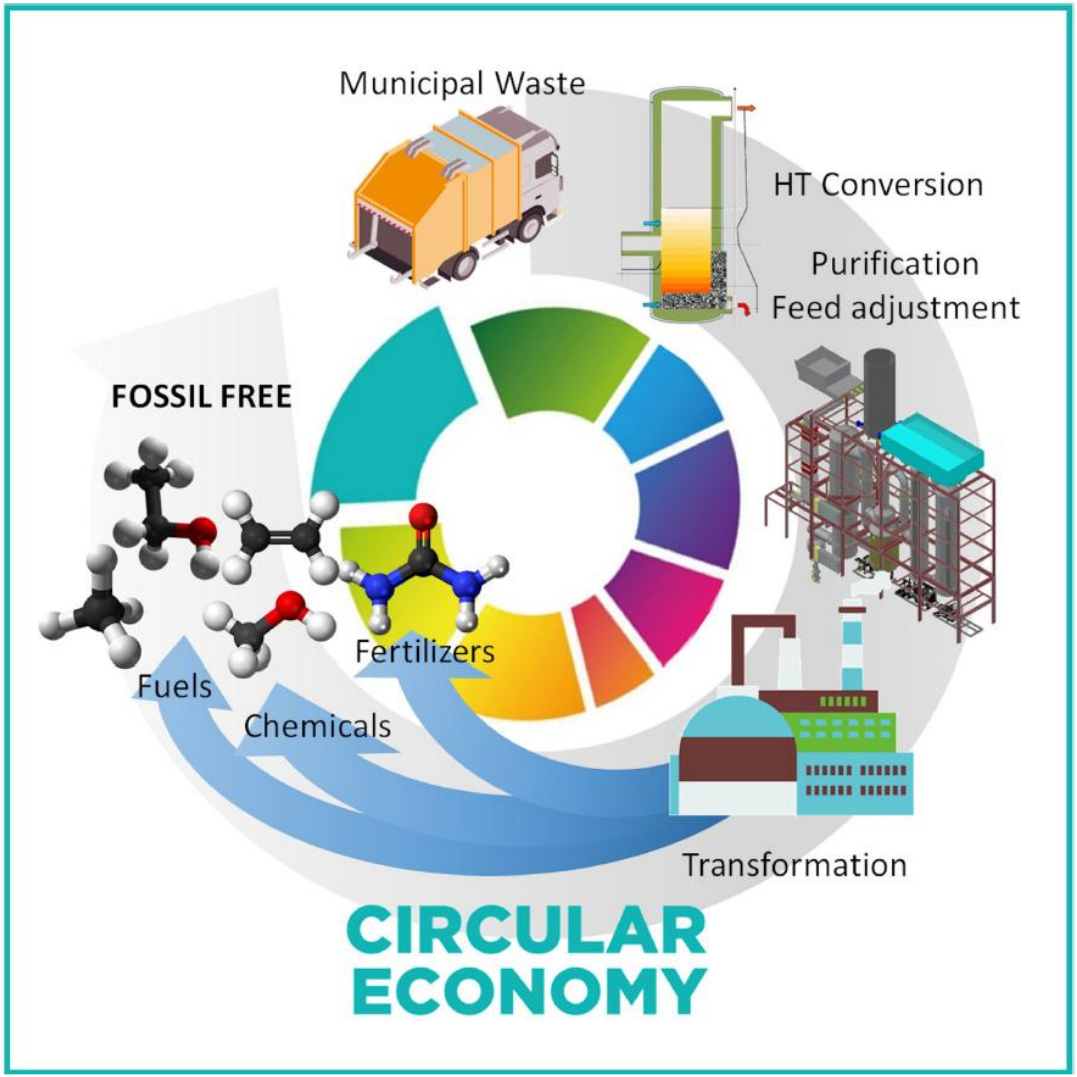
Chemical Recycling
With different methods, the material is broken down into chemical building blocks to make unsorted waste streams valuable for the chemical industry again.



https://lanxess.com/en/Responsibility/Societal-Added-Value/Circular-Economy

Circular Economy: the role of chemistry

Waste to chemicals



Waste to Chemicals for a Circular Economy
Gaetano Iaquaniello, Gabriele Centi, Annarita Salladini, Emma Palo, Siglinda Perathoner
https://doi.org/10.1002/chem.201802903

Circular Economy: the role of chemistry

Waste to chemicals

ChemPubSoc Europe
DOI: 10.1002/chem.201802903
CHEMISTRY A European Journal Concept
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Recycling

Waste to Chemicals for a Circular Economy

Gaetano Iaquaniello,[b, c] Gabriele Centi,*[a] Annarita Salladini,[b] Emma Palo,[c] and Siglinda Perathoner[d]

Wastes *and in particular municipal solid waste represent an untapped source of carbon (and hydrogen) to produce a large range of chemicals from methane to alcohols (as methanol or ethanol) or urea.*

- *Waste to chemicals*
- *Waste biorefiniery*
- *Waste to syngas (main challenge: process intensification)*

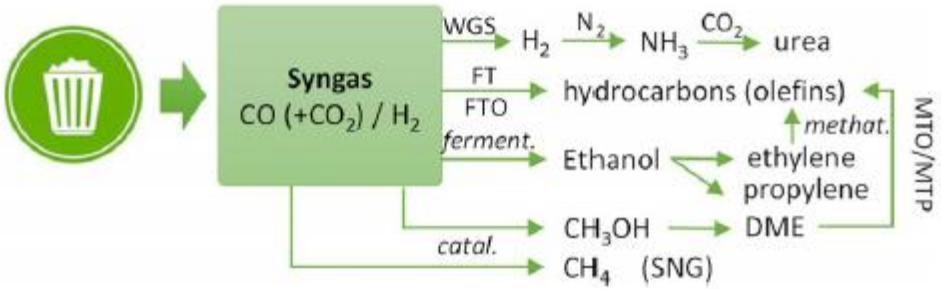
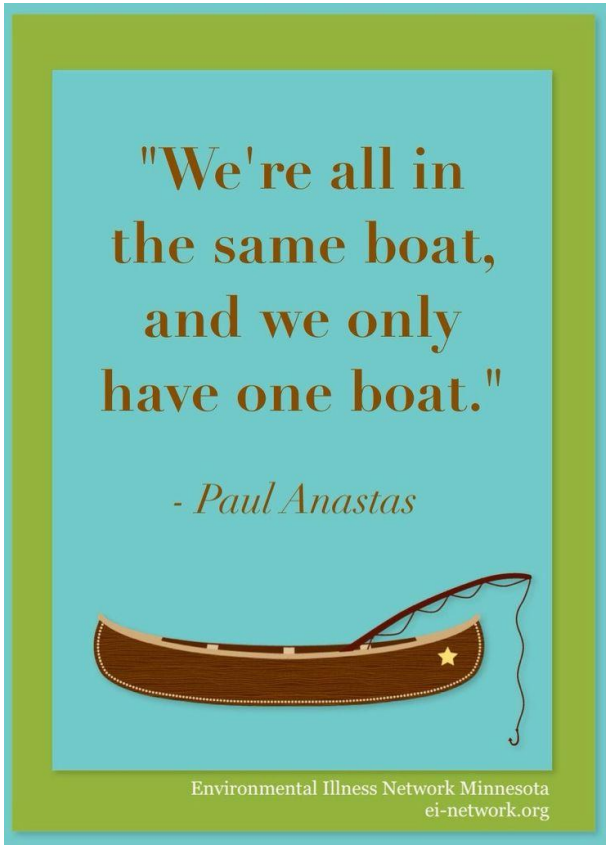


Figure 1. Versatility of syngas intermediate for chemical and fuels production. WGS: water gas shift; FT: Fischer–Tropsch process; FTO: Fischer–Tropsch to Olefins; *ferment*: gas fermentation; *methat.*: metathesis process; *catal.*: catalytic process; DME. dimethyl ether; SNG: substituted natural gas.

Green Chemistry

Green Chemistry definition

Sustainable and green chemistry in very simple terms is just a *different way of thinking about how chemistry and chemical engineering can be done*. Over the years different principles have been proposed that can be used when thinking about the design, development and implementation of chemical products and processes. These principles enable scientists and engineers to protect and benefit the economy, people and the planet by finding *creative and innovative ways to reduce waste, conserve energy, and discover replacements for hazardous (or critical) substances*.



https://www.acs.org/content/acs/en/greenchemistry

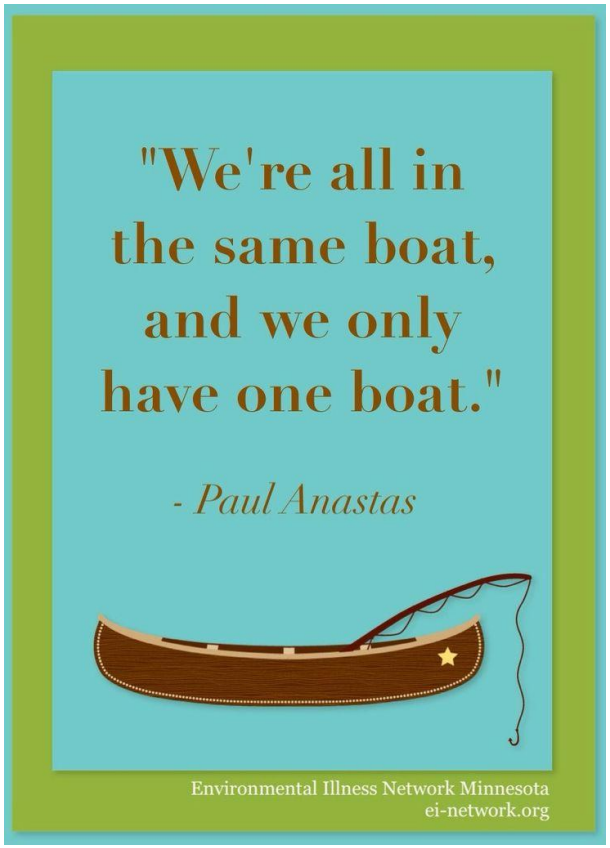
Green Chemistry

Green Chemistry definition

....it is a particular type of pollution prevention (no end-of-pipe approach)

....it is a fundamental methodology for changing the intrinsic nature of a chemical product or process so that it is inherently of less risk to human health and to the environment

....it involves the design and re-design of chemical synthesis and chemical products to prevent pollution



Green chemistry is the use of chemical principles and methodologies for source reduction of pollution

https://www.acs.org/content/acs/en/greenchemistry

12 principles of Green Chemistry (reminder from I year)

Box 1 | The twelve principles of green chemistry (GC)[8]

1. **Prevent waste.** It is better to prevent waste than to treat or clean up waste after it has been created.

2. **Maximise atom economy.** Chemical processes should maximize incorporation of all materials used into the final product.

3. **Less hazardous synthesis.** Chemical processes should avoid using or producing substances toxic to humans and the environment.

4. **Design benign chemicals.** Chemicals should be designed to achieve their function while minimizing their toxicity.

5. **Use safer solvents and auxiliaries.** Auxiliary substances should be rendered redundant wherever possible and harmless when used.

6. **Increase energy efficiency.** Energy requirements of chemical processes should be minimized.

7. **Use renewable feedstocks.** A raw material or feedstock should be renewable rather than depleting.

8. **Reduce chemical derivatives.** Reduce generation of derivatives, since such chemical steps require more reagents and produce additional waste.

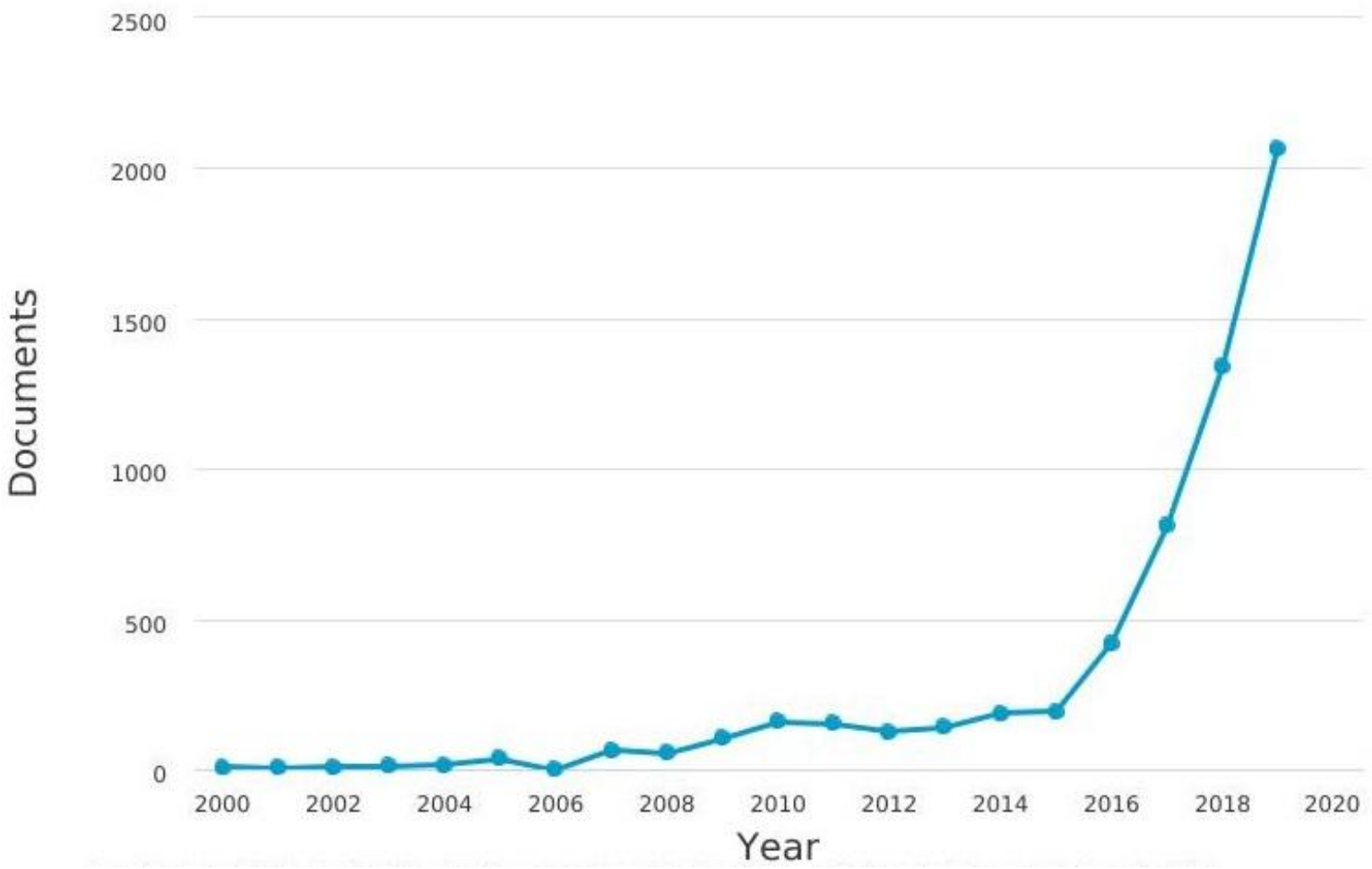
9. **Use catalytic (versus stoichiometric) conditions.** Using catalysts is preferable compared to using reagents in stoichiometric amounts.

10. **Design for degradation.** Chemical products should be designed to deteriorate after fulfilling a function without persisting in the environment.

11. **Real-time analysis for pollution prevention.** Analytical methods allow in-process monitoring and control prior to the formation of hazardous substances.

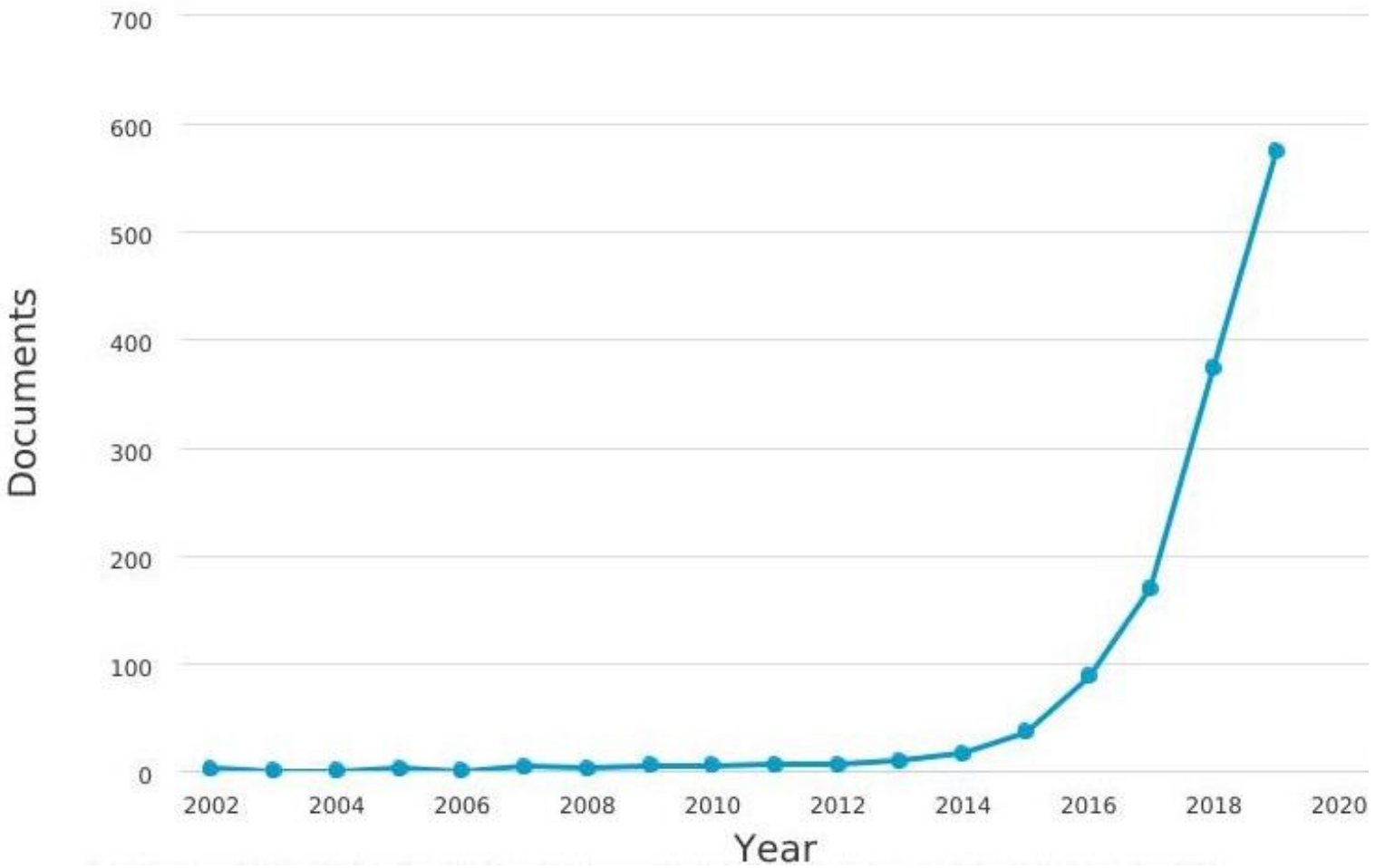
12. **Minimize potential for accidents.** Substances used in a chemical process should be chosen to minimize the potential for accidents.

Circular Economy and the Chemistry: the state of the art



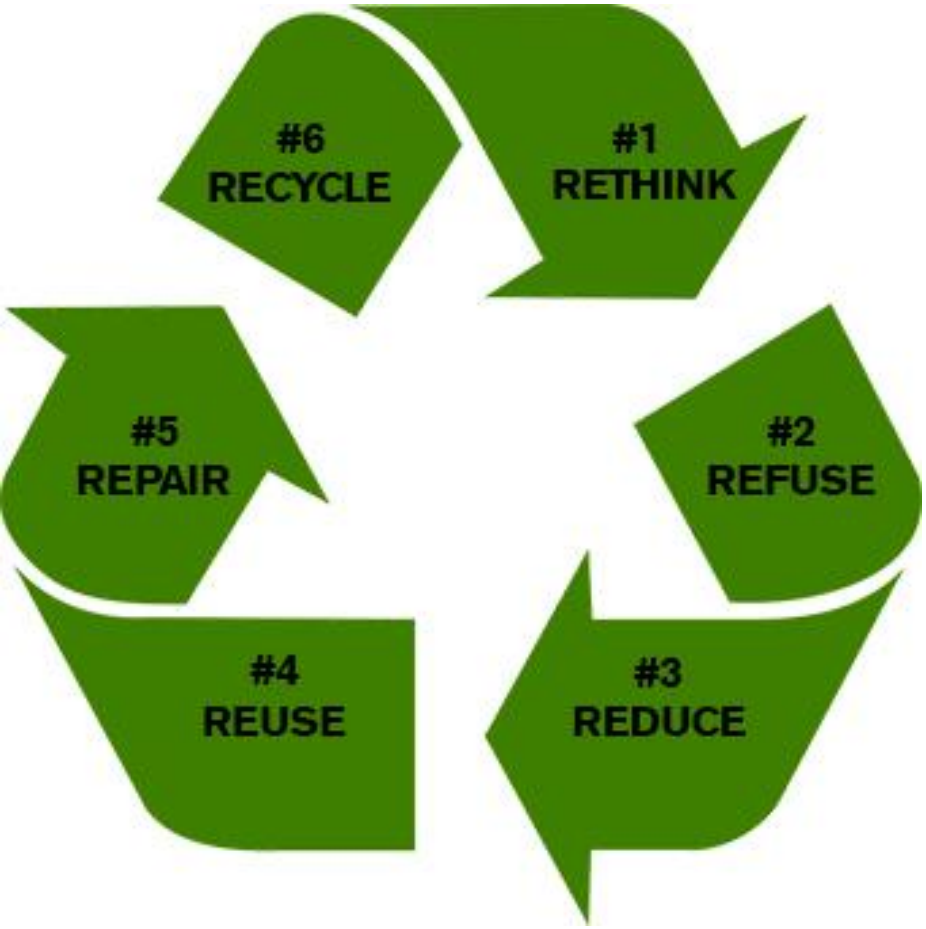
Number of published articles and reviews (timeframe 2000-2020) including “circular economy” in title, abstract, or keywords. Source: the Scopus database, www.scopus.com (accessed May 2020).

Circular Economy: the state of the art



Number of published articles and reviews (timeframe 2000-2020) including "circular economy" and refining with "chemistry" in title, abstract, or keywords. Source: the Scopus database, www.scopus.com (accessed May 2020).

The 6 «R» of Circular Economy



1. **Rethink: Is there a better way to solve this problem that is less harmful to the environment?**
2. Refuse: Not accepting things that are not the best option for the environment.
3. **Reduce: Is it possible to reduce the amount of material used to help protect valuable resources?**
4. Reuse: Can the product have another use? Can its parts be used in other products?
5. Repair: Is the product easy to repair?
6. **Recycle: Can materials in the product be recycled and used again?**

https://www.chalmers.se/en/areas-of-advance/production/research/sustainable-production/Pages/default.aspx

The birth of Circular Chemistry

The role of chemistry in the Circular Economy: circular chemistry

Circular chemistry to enable a circular economy

By expanding the scope of sustainability to the entire lifecycle of chemical products, the concept of circular chemistry aims to replace today's linear 'take–make–dispose' approach with circular processes. This will optimize resource efficiency across chemical value chains and enable a closed-loop, waste-free chemical industry.

Tom Keijer, Vincent Bakker and J. Chris Slootweg

Awareness of the finite nature of many resources — including the issue of element scarcity, shown in Fig. 1 — as well as the limited environmental tolerance towards our chemical industry has grown tremendously in the past few decades. It has become painfully obvious that the linear route of production, in which scarce resources are consumed and their value-added products are degraded to waste, is a route cause of several impending global crises such as climate change, diminished biodiversity, as well as food, water and energy shortages.

Advocates of the circular economy such as The Ellen MacArthur Foundation (https://www.ellenmacarthurfoundation.org) cleared the path for the emergence of novel policy frameworks that aim to redesign current economic systems, exemplified by the European Union's 2013 'manifesto for a resource-efficient Europe'. A circular economy is defined as "restorative and regenerative by design, and aims to keep products, components and materials at their highest utility and value at all times"[1]. Chemistry is crucial for achieving this[2–7]. Chemists understand their role in designing and developing indispensable materials and technologies, but also simultaneously recognize the potentially detrimental effects that this may have on their practice; they are therefore becoming increasingly aware that each step must be designed or reassessed with sustainability in mind.

Green chemistry for linear processes

Since it was first introduced in the 1980s, green chemistry has provided a framework for teaching and performing sustainable chemistry, and has delivered an impetus for developing cleaner products and processes[8–10] — which have enhanced chemical sustainability in industry and academia. Its twelve guiding principles (Box 1, GC 1–12) focus on the direct sustainability assessment of chemical reactions, and are perfectly suited for the optimization of linear production routes. The developments towards a circular economy, however, require a re-evaluation of what defines a sustainable chemical process, and needs to take into account the people, planet and profit level (referred to as the 'triple bottom line')[11]. Notably, innovative chemistry designed with sustainability in mind is only effective when translated into economically viable applications.

An illustrative example is the reported green synthesis of adipic acid — a key component for the manufacture of nylon-6,6 — by the direct oxidation of cyclohexene with hydrogen peroxide[12]. Solvent-free conditions are applied (GC 2), avoiding the use of the corrosive nitric acid (GC 3) and thus side-stepping the formation of the environmentally taxing gas nitrous oxide, N_2O — a waste product of the current industrial synthesis (GC 4). The green method, however, requires hydrogen peroxide, H_2O_2, as starting material, which means that this process is currently not commercially viable, since H_2O_2 is more expensive than the adipic acid product. Although this route obeys green chemistry principles, it violates the value chain. As a result, this green adipic acid synthesis has not been applied industrially, and has therefore not led to an overall increase in sustainability. Thus, accounting for the profit level of the triple bottom line is an essential component in the design of sustainable chemistry.

Other chemical processes may satisfy the green chemistry principles while being economically viable, yet remain unsustainable. For example, the Haber–Bosch process uses iron for the conversion of dinitrogen, N_2, into ammonia, NH_3, which in turn is used in the production of agricultural fertilizers. It is a key industry showcase for the use of catalysts (GC 9) in increasing energy efficiency (GC 6). The current process requires high temperatures and pressures, and further optimization has stagnated. After its use as fertilizer, large portions of the fixated nitrogen are lost to the environment, causing eutrophication, a global environmental concern, the importance of which should not be underestimated[13]. The cascade of environmental changes that results includes an increase in water and air pollution, both of which threaten to destabilize the Earth's system beyond the proposed 'planetary boundaries' or "safe operating space" for anthropogenic activities[14]. This highlights the importance of looking beyond the scientific discovery and analysing the global impact of chemistry using a systems approach[15].



Credit: European Parliament

Circular chemistry for sustainability

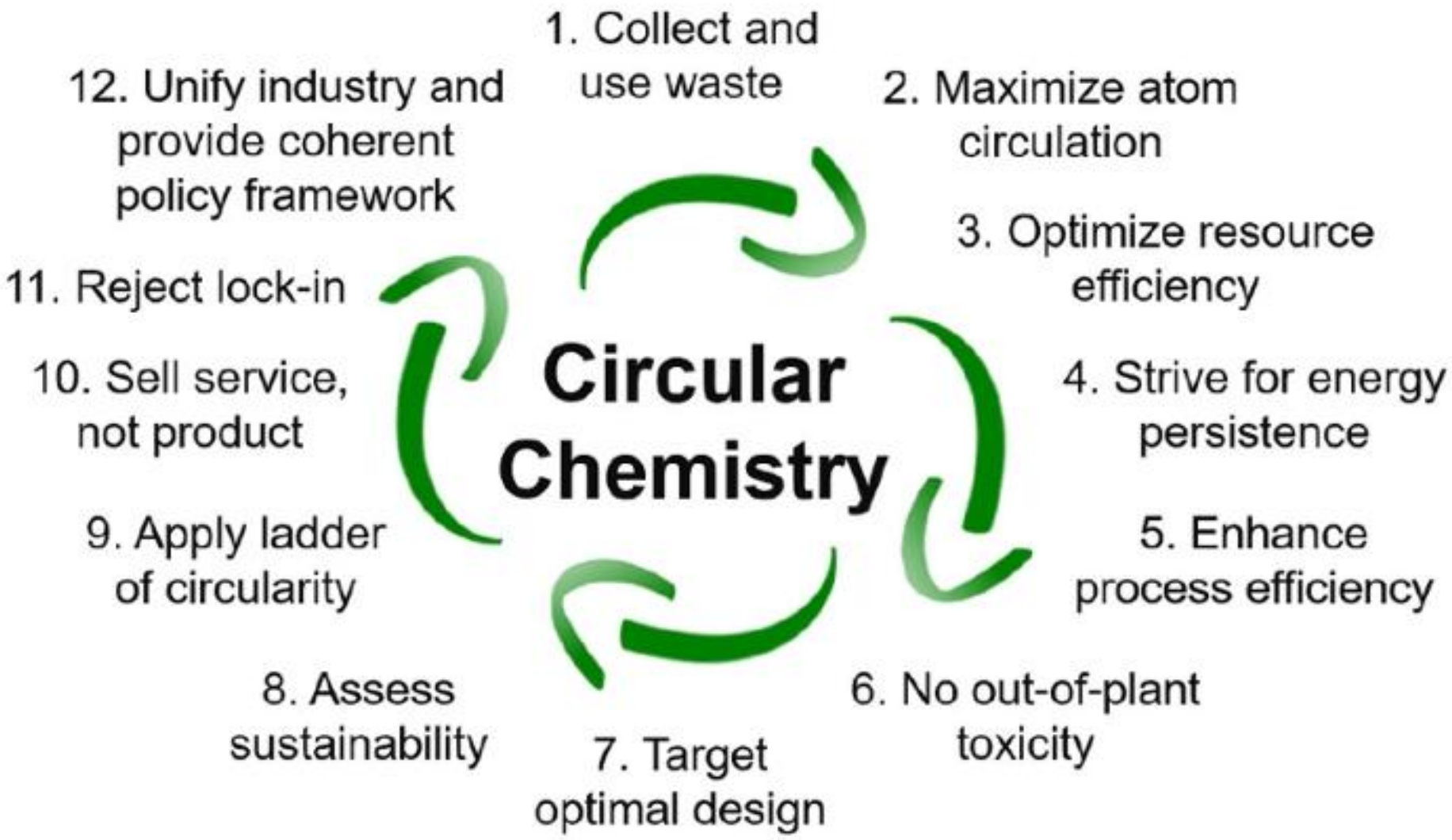
In this Comment, we provide a holistic view on how chemistry can contribute to the development of a circular economy, and formulate twelve principles for a 'circular chemistry' (Fig. 2 and Box 2, CC 1–12). In doing so, we provide a framework analogous to that of green chemistry, which has been adapted to facilitate the transition to a circular economy. This approach aims to make chemical processes truly circular by expanding the scope of sustainability from process optimization to the entire lifecycle of chemical products. It promotes, in particular, resource efficiency across chemical value chains and highlights the need to develop novel chemical reactions to reuse and recycle chemicals, to in turn enable development towards a closed-loop, waste-free chemical industry[16–19].

Waste is a resource

Regarding waste as a resource is a prerequisite for circularity. Redirecting

Circular chemistry to enable a circular economy
T. Keijer, V. Bakker, J. C. Slootweg
Nature Chemistry, 11, 2019, 190

12 paradigms of circular chemistry



12 principles of Circular Chemistry

Box 2 | The twelve principles of circular chemistry (CC)

1. Collect and use waste. Waste is a valuable resource that should be transformed into marketable products.

2. Maximize atom circulation. Circular processes should aim to maximize the utility of all atoms in existing molecules.

3. Optimize resource efficiency. Resource conservation should be targeted, promoting reuse and preserving finite feedstocks.

4. Strive for energy persistence. Energy efficiency should be maximized.

5. Enhance process efficiency. Innovations should continuously improve in- and post-process reuse and recycling, preferably on-site.

6. No out-of-plant toxicity. Chemical processes should not release any toxic compounds into the environment.

7. Target optimal design. Design should be based on the highest end-of-life options, accounting for separation, purification and degradation.

8. Assess sustainability. Environmental assessments (typified by the LCA) should become prevalent to identify inefficiencies in chemical processes.

9. Apply ladder of circularity. The end-of-life options for a product should strive for the highest possibilities on the ladder of circularity.

10. Sell service, not product. Producers should employ service-based business models such as chemical leasing, promoting efficiency over production rate.

11. Reject lock-in. Business and regulatory environment should be flexible to allow the implementation of innovations.

12. Unify industry and provide coherent policy framework. The industry and policy should be unified to create an optimal environment to enable circularity in chemical processes.

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Circular chemistry to enable a circular economy, T. Keijer, V. Bakker, J. C. Slootweg Nature Chemistry, 11, 2019, 190

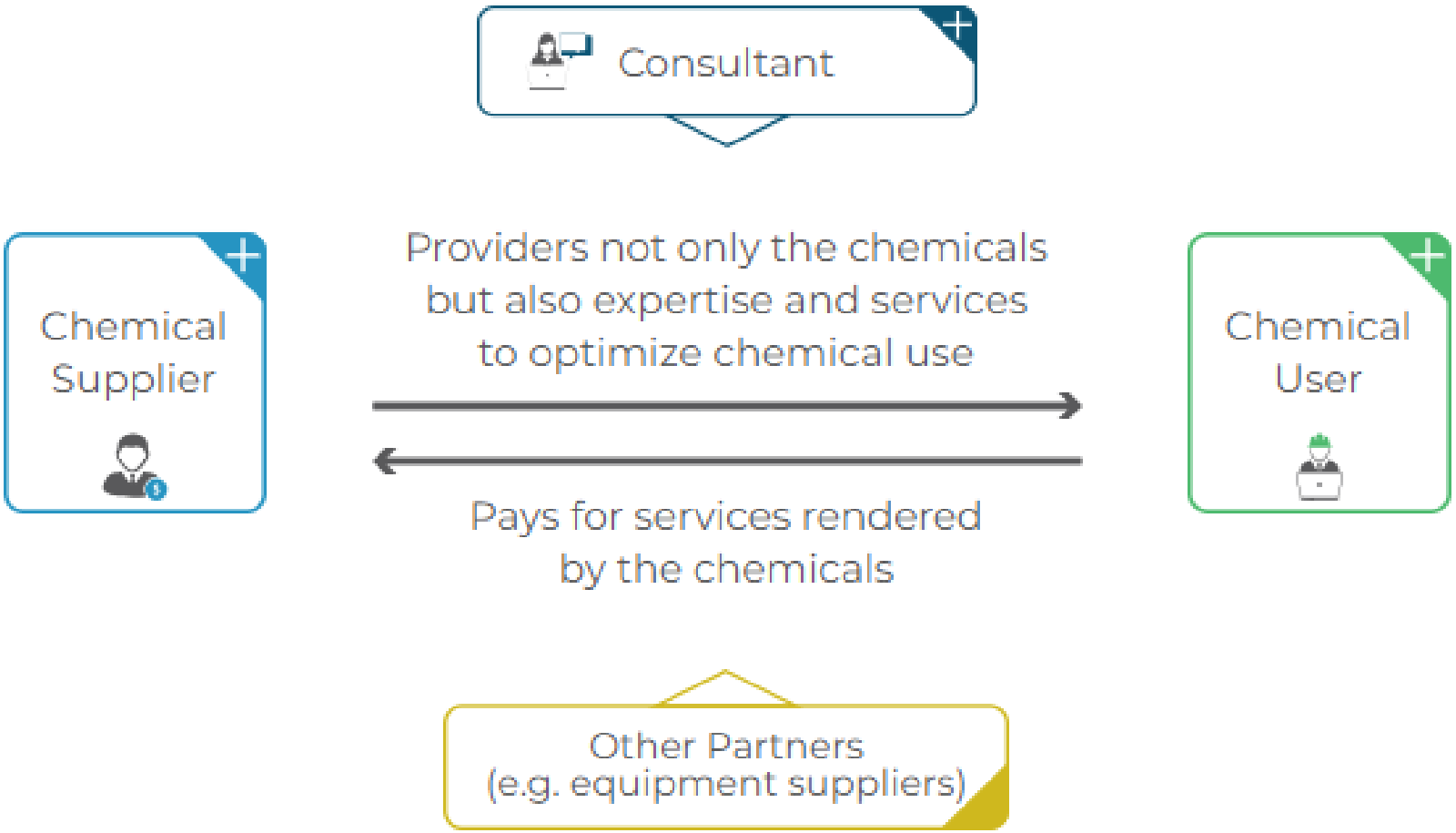
Chemical leasing

Chemical Leasing is based on an alternative approach that turns the business model upside down: profit doesn't depend on more volume, but less. At the heart of the model is the idea that economic success no longer depends on the volume of chemicals sold, but on the service that is linked with the chemicals. Chemical consumption becomes a cost rather than a revenue factor. The business partners and the environment shall benefit from the co-creation of jointly developed resource-efficient and innovative solutions and fair profit-sharing.

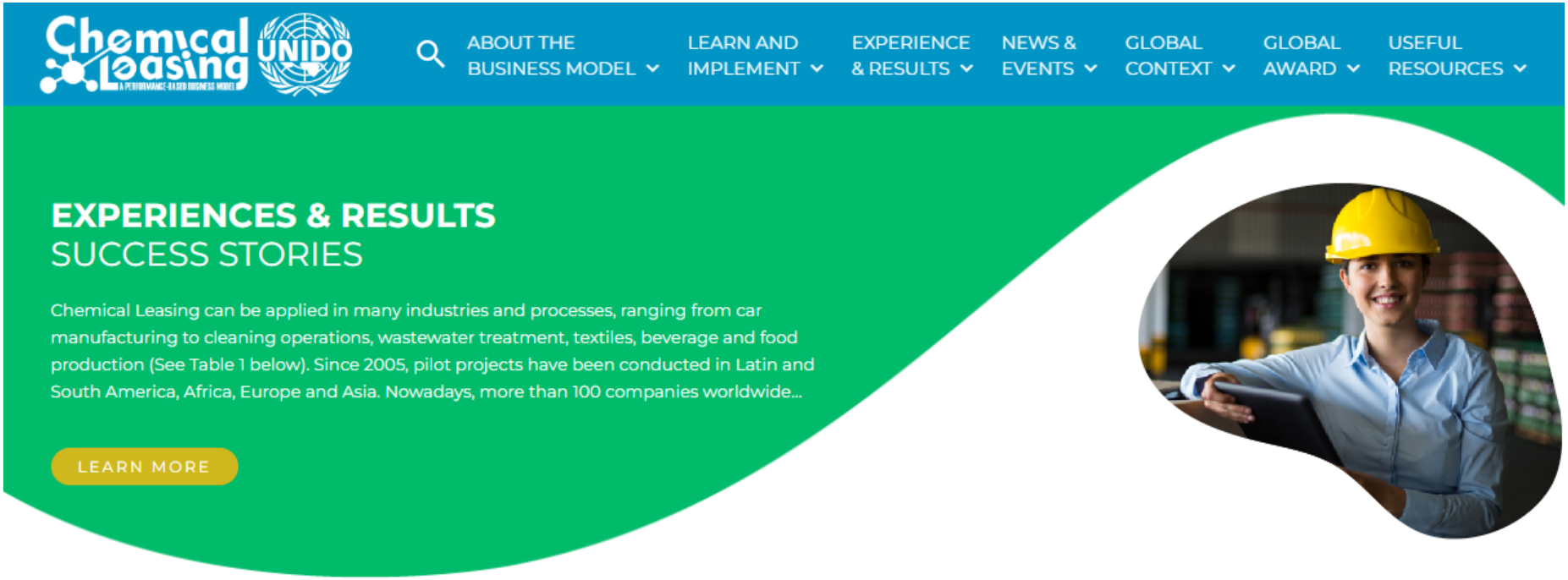
https://chemicalleasing.org (UNIDO)
See article on https://www.renewablematter.eu/la-prestazione-come-prodotto-il-modello-del-chemical-leasing

- in this business model it is the service provided by that chemical that is paid for, (e.g. volume of water treated, number of articles painted) and not the quantity of chemicals purchased.
- with efficiency rewarding the supplier instead of material consumption, waste reduction is achieved.
- UNIDO (UN Industrial Development Organisation) claims that, by decoupling payment from consumption, chemical leasing encourages better management of chemicals with beneficial consequences for the environment
- in a service based business model there is a clear economic incentive to reduce material use and increase product efficiency and longevity

Chemical leasing



Chemical leasing



https://chemicalleasing.com/

United Nations Industrial Development Organization: UNIDO

Chemical leasing

United Nations Industrial Development Organization
Vienna

UNIDO RECP Study

Chemical Leasing within industrial and service sector cleaning operations

A viable business model with potential to reduce chemical use and negative environmental impacts

Chemical leasing: cleaning

Variable	Examples
Technical results	• Stable level of quality achieved (formerly decreasing level of quality by time) (1 case) • More efficient cleaning process and concrete monitoring system
Safety results	• System for hazardous waste management (1 case) • Toxic fumes eliminated by chemical substitution • Employees not in contact with solvent due to closed system (1 case) • Awareness raised with operating personnel of chemical hazards
Environmental results	• Waste reduced by 94% per year • Waste reduced by 60% per year • Solvent waste reduced by more than 25 t/year • 20% more solvent waste collected • VOC emission reduction by 60% (100 ppm ➔ 40 ppm)

Financial results and resource efficiency	• The use of cleaning chemicals reduced with 75%
	• Savings for customer (2 cases) 10-15%
	• Savings per cleaned item 33% and more
	• Energy consumption reduced by 50%
	• Fuel consumption reduced by 16% per year
	• Electricity savings
	• Water consumption reduced by 88%
	• Extended the lifespan of the chemicals in use
	• Use of spare parts reduced by 66%
	• Reduction in solvent consumption by
	  ○ 20 tonnes/ year (absolute level only reported)
	  ○ Ranges included: 10%; 8–10%; 23%; 71%; 75%
	  ○ perchloroethylene 83% = 25 t/year

Chemical leasing

Industrial sectors	Chemicals identified (selection)
Manufacture of electronic equipment	Powder coatings
Manufacture of fabricated metal products	Organic solvents, detergents
Various industries/steel treatment	Galvanizing and phosphating agents
Beverage production	Lubricants for packaging conveyors
Waste water and drinking water treatment	Water treatment chemicals
Accommodation and service sector	Cleaning chemicals
Beverage and food processing	Glues, adhesives, detergents, sanitizing chemicals
Petrochemical industry	Catalysts and water treatment chemicals
Printing industry	Ink, printing chemicals

https://chemicalleasing.com/success-stories/

Chemical leasing

Table 1 Specific examples of chemical leasing projects[15]

Process	Country	Payment	Benefits
Metal cleaning	Austria	Per number of parts cleaned	Volume of solvent reduced by 71%, energy consumption halved.
Waste water treatment	Columbia	Per cubic metre of water	Chemical consumption halved.
Dyeing	India	Per kilogram of textiles	Annual savings: 2 million kWh of energy, 78 tonnes of dyes, 75 million litres of water.
Painting	Sri Lanka	Per area of building painted	Material use 10% more efficient. Reductions in water use and packaging also achieved.
Machine lubrication	Serbia	Per hour of operation	Hazardous chemicals replaced, and 6.5 million litres of water saved.

Source of the table: Green Chem., 2016, 18, 3914–3934

For example, the function of the chemical could be to clean or degrease metal parts, or to protect a surface. Payment is then made according to functional units, that is, the number of pieces cleaned or the extent of area coated (www.chemicalleasing.org)

Circular Economy and the role of Chemistry

SYNTHETIC CHEMISTRY

Rethinking chemistry for a circular economy

Chemical complexity complicates product recycling and manufacturing sustainability

By Klaus Kümmerer[1,2], James H. Clark[3], Vânia G. Zuin[3,4]

Green Chemistry

PERSPECTIVE

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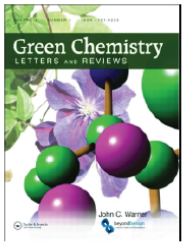
Cite this: *Green Chem.*, 2016, **18**, 3914

Circular economy design considerations for research and process development in the chemical sciences

James H. Clark,* Thomas J. Farmer, Lorenzo Herrero-Davila† and James Sherwood



Green Chemistry Letters and Reviews

ISSN: 1751-8253 (Print) 1751-7192 (Online) Journal homepage: https://www.tandfonline.com/loi/tgcl20

Ripe for disruption: reimagining the role of green chemistry in a circular economy

Mats Linder

Rethinking chemistry

- most of today's chemical products: synthetic, based on non renewable resources, and formed into complex articles such as plastics.
- recovering molecular value requires a considerable investment in funding and energy.
- keeping the chemical structure of the final product and its building blocks (form, composition, stereochemistry, and functional groups) as similar as possible to the starting material is desirable for both virgin and recycled materials.
- future products must constrain the levels of complexity of their constituent resources and not change them in recycling.
- this will aid subsequent recycling and reduce the number of downstream chemical processes and unit operations, as these cause waste production, entropy increase, and resource consumption, including energy.

Rethinking chemistry

- final products should be as simple in composition as possible, minimising additives and avoiding toxic components and elements not easily separated for recovery.
- to avoid mixing varying constituents and increasing unnecessary complexity, flows of products and their constituents must be kept as separate as possible at all stages of their life cycle, from resource extraction and synthesis to use and recycling. If the flows are highly variable, recycling will be hindered (e.g. biomass).
- similarly, local flows are preferable to global ones, and more complete knowledge of the composition of materials and products will help with speedy recycling (e.g. “chemical passport”).
- it is necessary to locate waste streams and decipher how to collect them, or they might be lost forever. (e.g. relevance of rational sorting/tracking technologies)

Rethinking chemistry

1. Keep molecular complexity to the minimum required for the desired performance, including end of life (complex molecules require more synthesis steps, may have additional undesirable properties, and can be more difficult to recycle).
2. Design products for recycling, including all additives and other components of the product.
3. Reduce and simplify diversity and dynamics of substance, material, and product flows; e.g., use fewer chemicals overall (both number and quantity), design for less resource intensity, and adapt innovation speed of products to adaptation speed of recycling.
4. Avoid complex products (e.g., multiple components, materials).
5. Minimise use of product components that cannot easily be separated and recycled (e.g., solvents, metals).
6. Design products not suitable for capture and recycling for complete fast mineralization at the end of their lives (e.g., pharmaceuticals, pesticides, personal care and cleaning products).
7. Prevent raw materials from becoming critical through reduced use and efficient recovery and recycling (e.g., many metals).
8. Avoid entropic losses and transfers (e.g., dissipation of metals, energy).
9. Avoid rebound effects (e.g., using less carbon often means higher demand for metals).
10. Be responsible for/develop ownership of your product throughout its complete life cycle, including recycling.
11. Ensure traceability and consider use of product digital passports (e.g., composition of products, components, and processes).
12. Develop and apply circular metrics (e.g., giving credit to the use of by-products).
13. Change traditional chemical practices based on “bigger-faster” into “optimal adapted-better-safer” and change ownership to rent, lease, and share business models.
14. Keep processes as simple as possible with a minimum number of steps, auxiliaries, energy, and unit operations (e.g., separations, purification).
15. Design processes for optimal material recovery of auxiliaries, unused substrates, and unintended by-products (based on quality and quantity).



SYNTHETIC CHEMISTRY

Rethinking chemistry for a circular economy

Chemical complexity complicates product recycling and manufacturing sustainability

By Klaus Kümmerer[1,2], James H. Clark[3], Vânia G. Zuin[3,4]

desired grade, structure, and function for an application. With today's diverse and inter-

products have a long lifetime, such as those used in the human-made environ-

Rethinking chemistry

1. Keep molecular complexity to the minimum required for the desired performance, including end of life (complex molecules require more synthesis steps, may have additional undesirable properties, and can be more difficult to recycle).
2. Design products for recycling, including all additives and other components of the product.
3. Reduce and simplify diversity and dynamics of substance, material, and product flows; e.g., use fewer chemicals overall (both number and quantity), design for less resource intensity, and adapt innovation speed of products to adaptation speed of recycling.
4. Avoid complex products (e.g., multiple components, materials).
5. Minimise use of product components that cannot easily be separated and recycled (e.g., solvents, metals).
6. Design products not suitable for capture and recycling for complete fast mineralization at the end of their lives (e.g., pharmaceuticals, pesticides, personal care and cleaning products).
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*EPR: Extended producer responsibility



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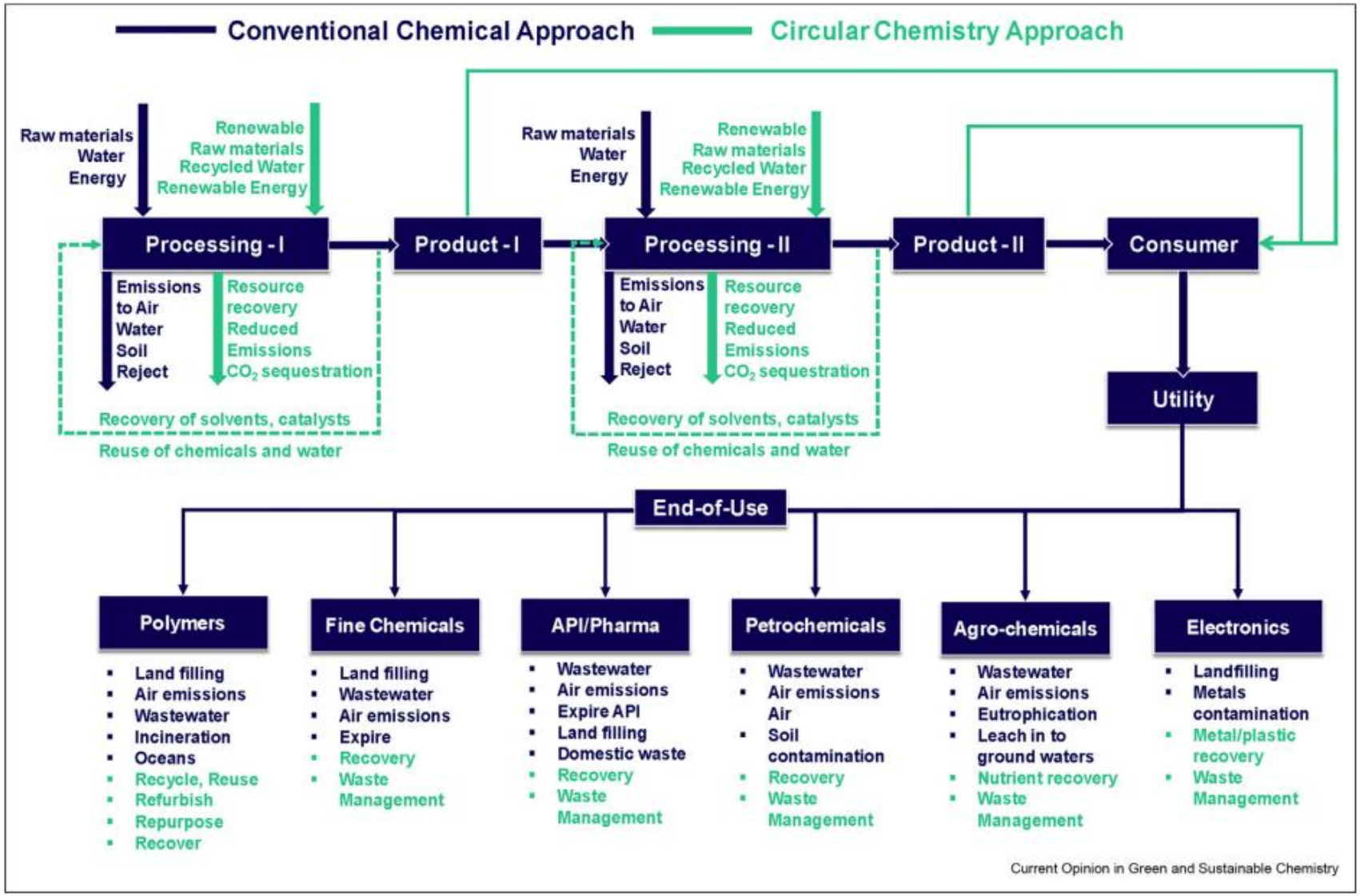
Rethinking chemistry



Current Opinion in Green and Sustainable Chemistry 2021, 28:100434

EPR

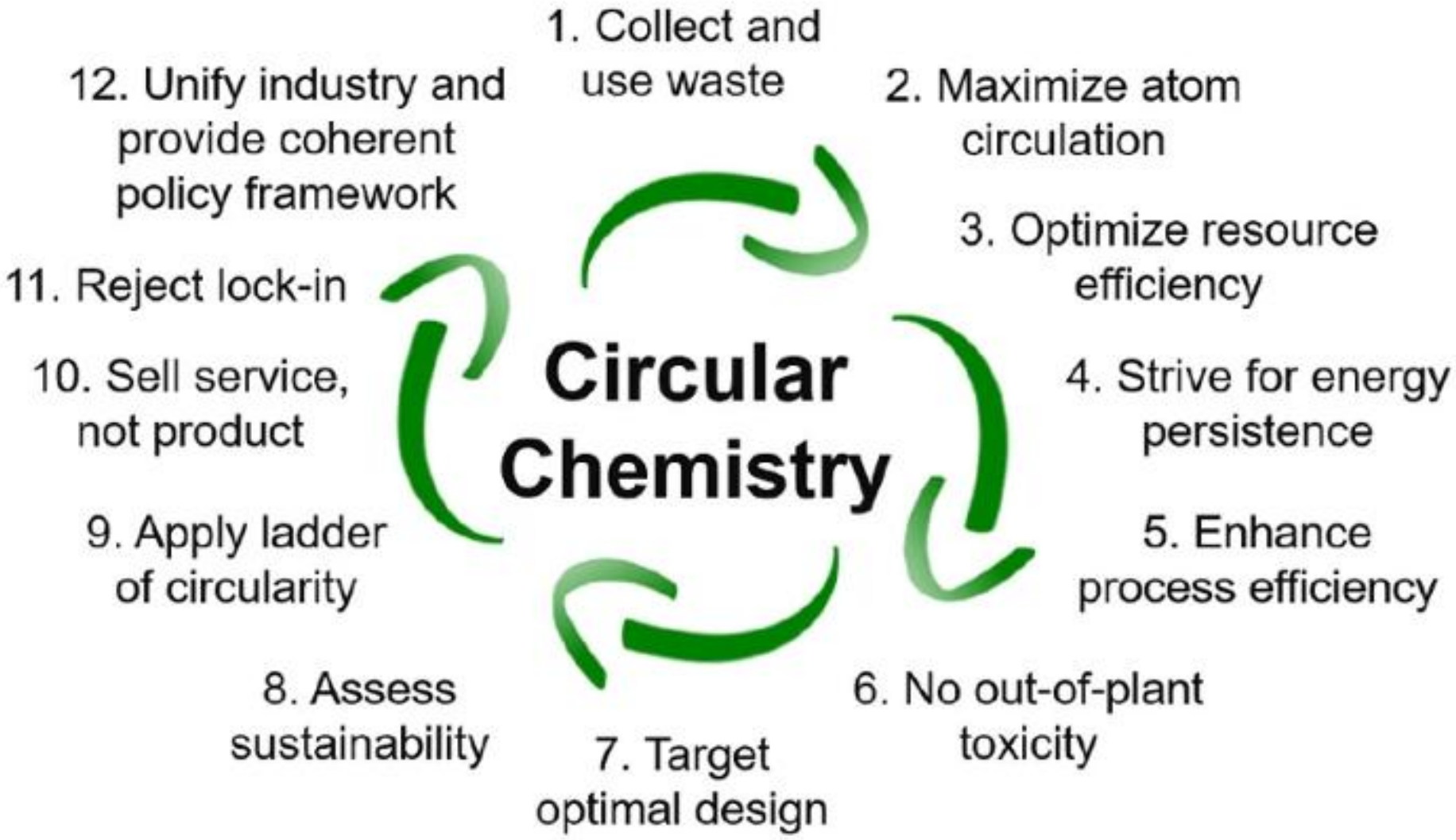
Extended producer responsibility (EPR) can be defined as "an environmental policy approach in which a producer's responsibility for a product is extended to the post-consumer stage".

Source: https://ec.europa.eu/environment/archives/waste/eu_guidance/introduction.html

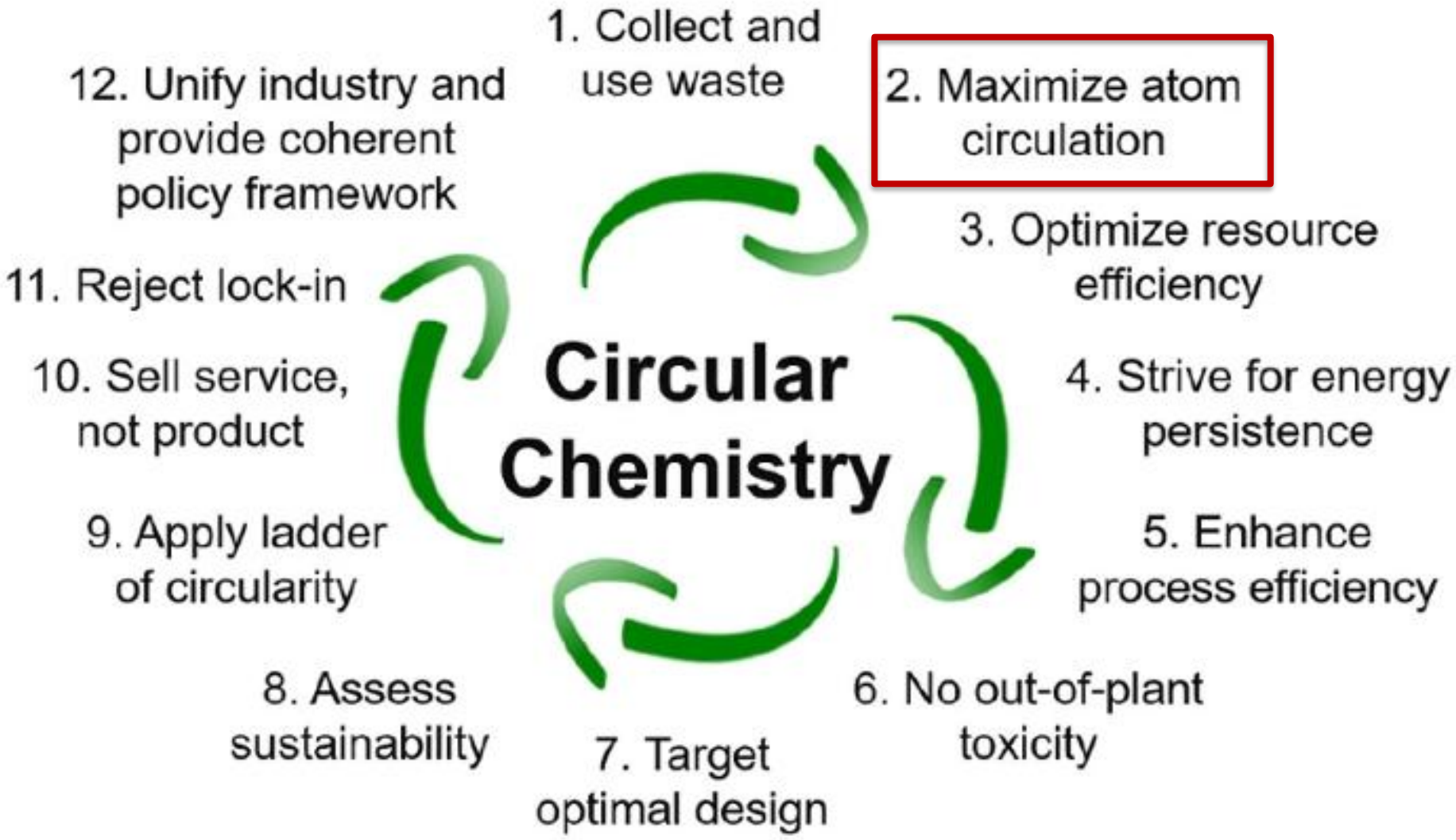
Extended Producer Responsibility (EPR) is an environmental policy that makes producers responsible for the entire life cycle of the products that they introduce on the market, from their design until end of life (including waste collection and recycling). Under EPR regulations, liable companies must mitigate the environmental impacts of their products throughout the entire product life cycle.

see Interactive Seminar by Landbell in a.a. 2022-2023

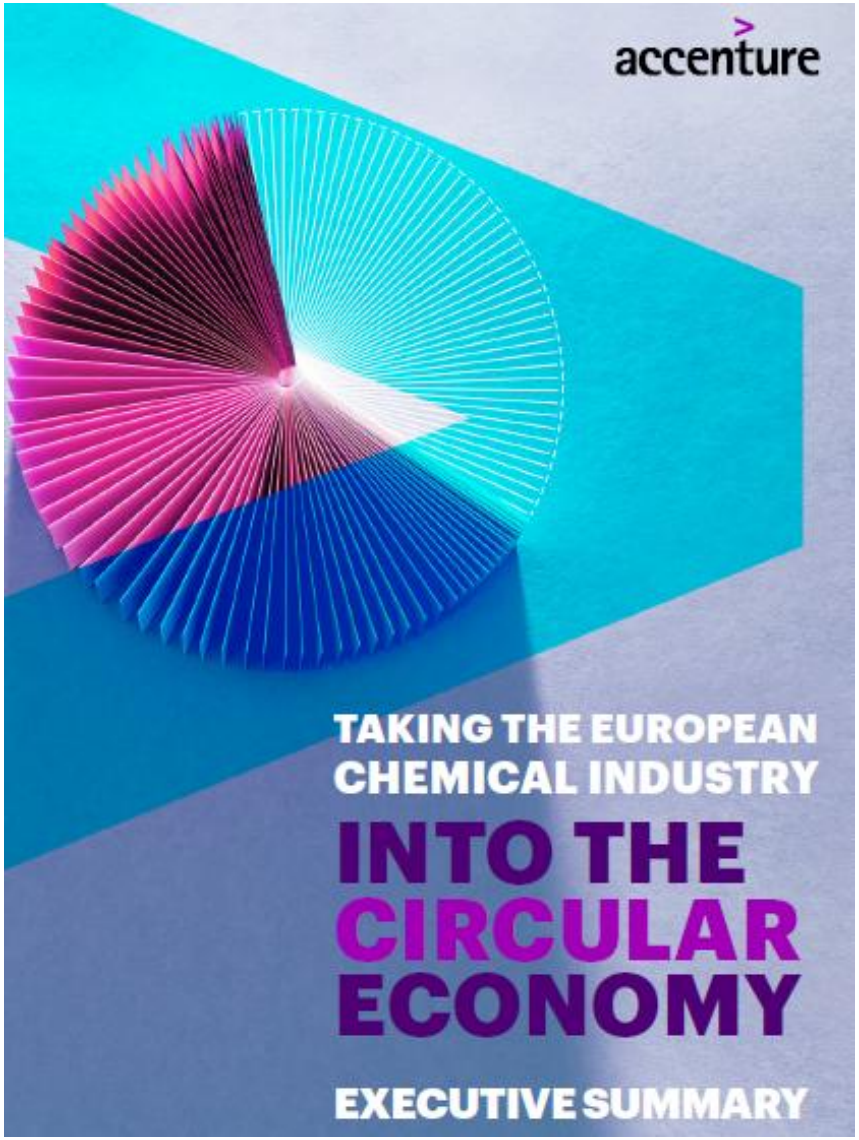
Examples of circular chemistry



Examples of circular chemistry



Circular Economy and the role of Chemistry



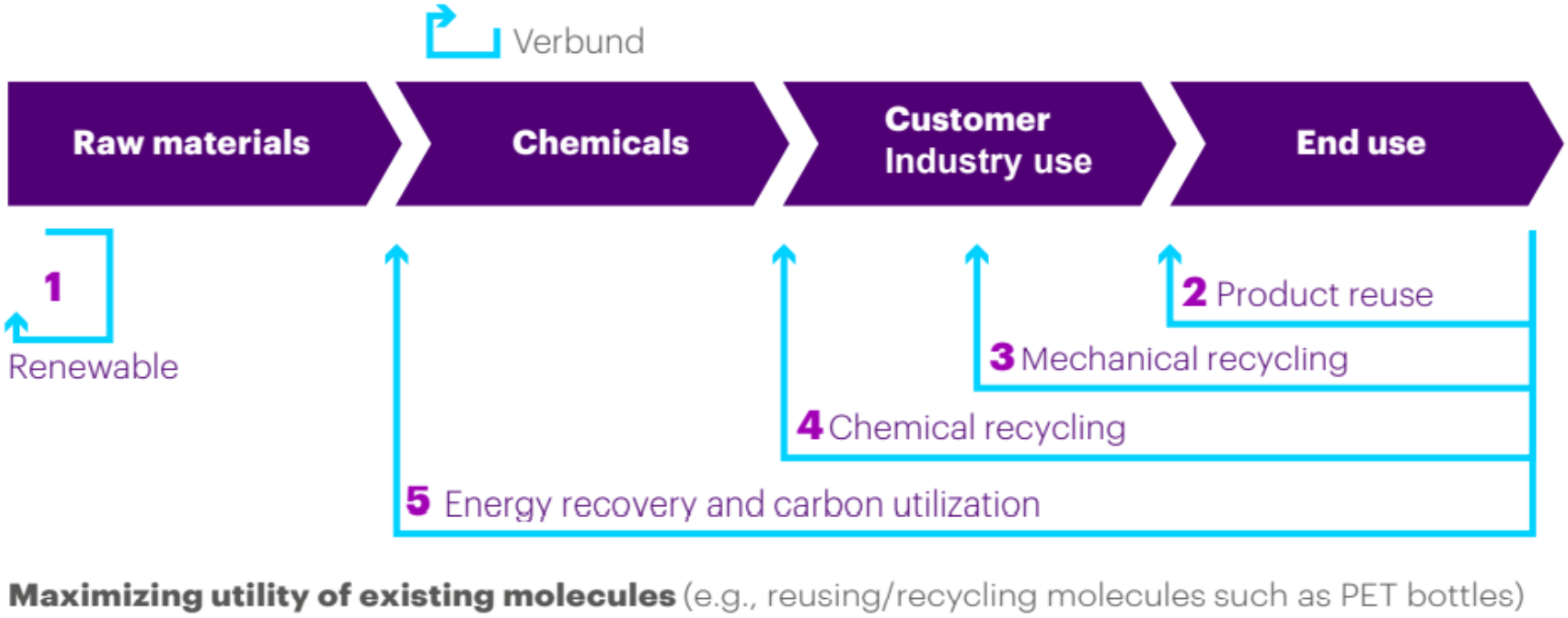
To understand the impact that the circular economy could have on the European chemical industry, it is useful to look at the issue from two perspectives:

1. circulating molecules and
2. enabling the circular economy in downstream industries.

Examples of circular chemistry applications

2. Maximize atoms/molecules circulation

As the term suggests, circulating molecules means reusing existing molecules—in either the form of hydrocarbons contained in biomass or in the form of chemical material contained in end-consumer products.

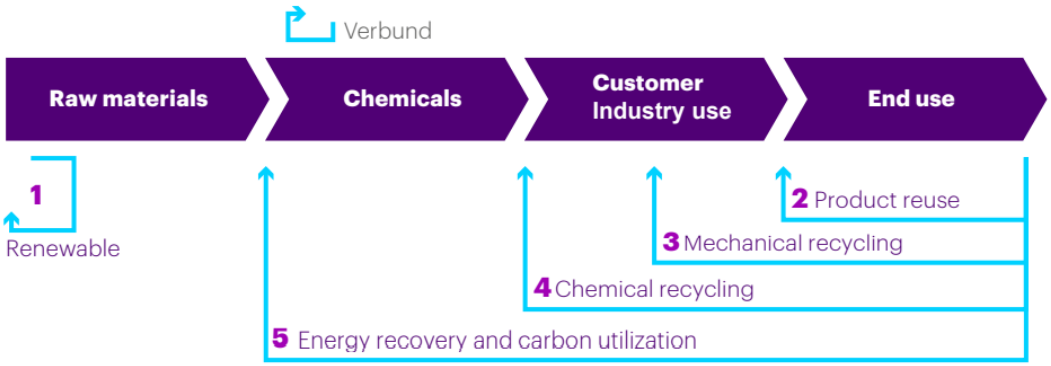


Maximizing utility of existing molecules (e.g., reusing/recycling molecules such as PET bottles)

Souce of the picture: Taking the European Chemical Industry into the Circular Economy Accenture & CEFIC (https://cefic.org/app/uploads/2019/02/Accenture-Cefic-circular-economy-brochure.pdf, open access on line)

Examples of circular chemistry applications

- As more existing molecules are circulated, the less need there might be to produce chemical precursors from fossil-based raw materials.
- In an ambitious scenario, up to 60 percent of the molecules provided by the European chemical industry to its customers can be recirculated, assuming sufficient and cost-competitive energy is accessible, the necessary logistics infrastructure is in place, and abundant capital is available for the needed investments.
- This level of recycling could be accomplished through the maximized use of five molecule-circulating loops in the industry:
- **Loop 1**: Circularity based on renewable feedstock
- **Loop 2**: Circularity based on increased reuse of products containing chemical industry outputs
- **Loop 3**: Circularity based on molecule reuse (mechanical recycling)
- **Loop 4**: Circularity based on modification of molecules and reuse as precursors (chemical recycling)
- **Loop 5**: Circularity based on energy recovery and reuse of CO_2



Maximizing utility of existing molecules (e.g., reusing/recycling molecules such as PET bottles)

Examples of circular chemistry applications

DETAILS ON THE MODEL FOR MOLECULES CIRCULATION CALCULATION (for in depth)

In this model, Accenture calculates that 92 Mt of feedstock are converted into 107 Mt of basic chemicals, which are converted into 117 Mt of intermediate chemicals, which are finally turned into 106 Mt of output chemicals for sale to customers.

Even though the same carbon atoms travel through this chain, volumes at each step differ for stoichiometric reasons.

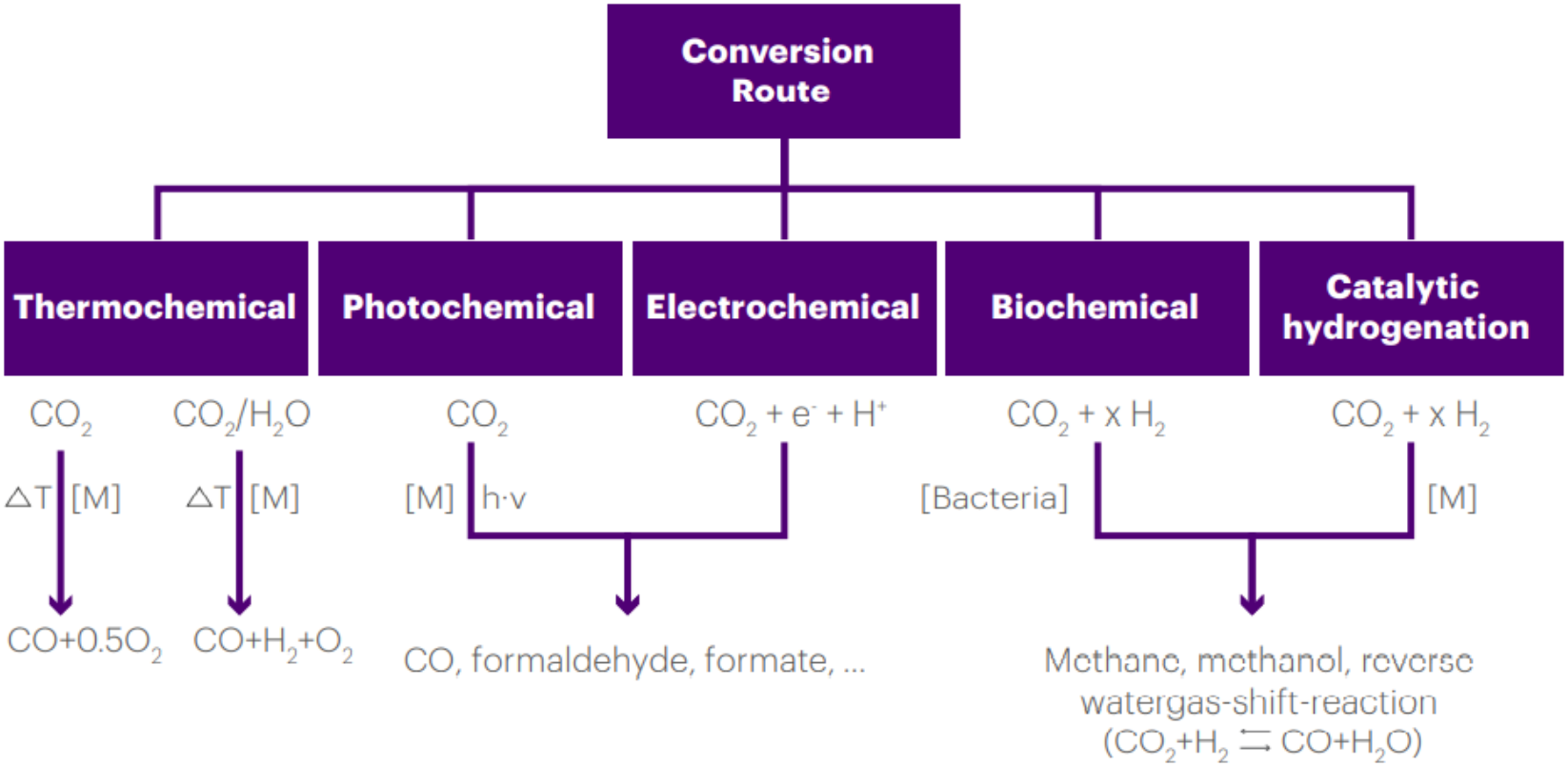
The production output of the European chemical industry is typically reported in aggregate numbers across those three steps, resulting in a total production volume of 330 Mt.

Accenture has then calculated the amount of current feedstock that could be replaced with renewable feedstock (Loop 1), and how much of the 106 Mt of chemical output at the end of the described chain could be looped back (Loops 2-5).

Taking the European Chemical Industry into the Circular Economy Accenture & CEFIC (https://cefic.org/app/uploads/2019/02/Accenture-Cefic-circular-economy-brochure.pdf, open access on line)

Examples of circular chemistry applications

Loop 5: Overview of CO_2 conversion route



Source: G. Centi, S. Perathoner and G. Iaquaniello: Realizing Resource and Energy Efficiency in Chemical Industry by Using CO2 , Springer-Verlag, London 201

Examples of circular chemistry applications

Loop 5: Overview of CO_2 conversion route: CHALLENGES

1. carbon capture and utilization challenging/demanding

2. required new assets for creating dense CO_2 sources (hotspots) and for re-synthesizing carbon into hydrocarbons

3. establishment of reliable hydrogen supply at large scale (note: by combustion, one ton of hydrocarbon creates 3.1 tons of CO_2 on average; regeneration by hydrogenation back to hydrocarbons requires 0.6 tons of hydrogen. Hence, for the assumed 10 Mt of molecule circulation through Loop 5, this would imply a hydrogen requirement of 6 Mt).

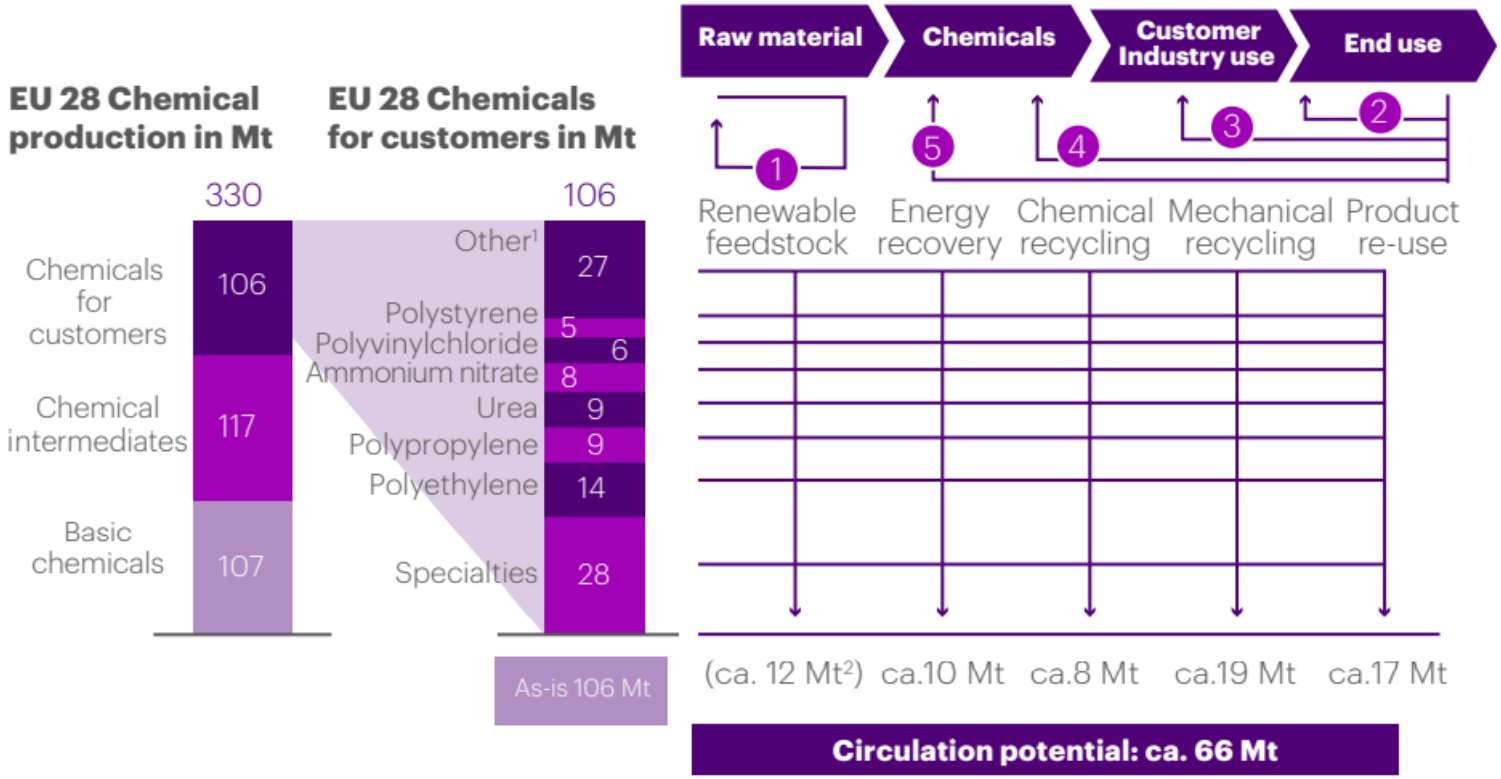
4. Carbon-neutral sources of energy must be used to generate the energy required for the hydrogen production, as the usage of energy generated with fossil fuel would more than offset the saved CO_2 emissions

Source: G. Centi, S. Perathoner and G. Iaquaniello: Realizing Resource and Energy Efficiency in Chemical Industry by Using CO2 , Springer-Verlag, London 201

Examples of circular chemistry applications

The five loops' impact on the circulation of molecules

Out of 106 Mt chemicals delivered to customers, up to 60% can be circulated



Taking the European Chemical Industry into the Circular Economy Accenture & CEFIC (https://cefic.org/app/uploads/2019/02/Accenture-Cefic-circular-economy-brochure.pdf, open access on line)

Circular Economy: the role of chemistry

Our contribution

Chemistry–A European Journal
Essays
doi.org/10.1002/chem.202002844
Eur
Europ
Socie

Inorganic Chemistry

Enabling Circular Economy: The Overlooked Role of Inorganic Materials Chemistry

Gabriella Salviulo,[a, b] Maria Cristina Lavagnolo,[c] Manuele Dabalà,[d] Enrico Bernardo,[d] Antonino Polimeno,[e] Mauro Sambi,[e] Franco Bonollo,[f] and Silvia Gross*[e]

Invited Essay

Chem. Eur. J., 2021, 27, 6676

Circular Economy: the role of chemistry

Our contribution

Specific aspects where the role of (inorganic) chemistry will be increasingly relevant in the implementation of circular models in production are:

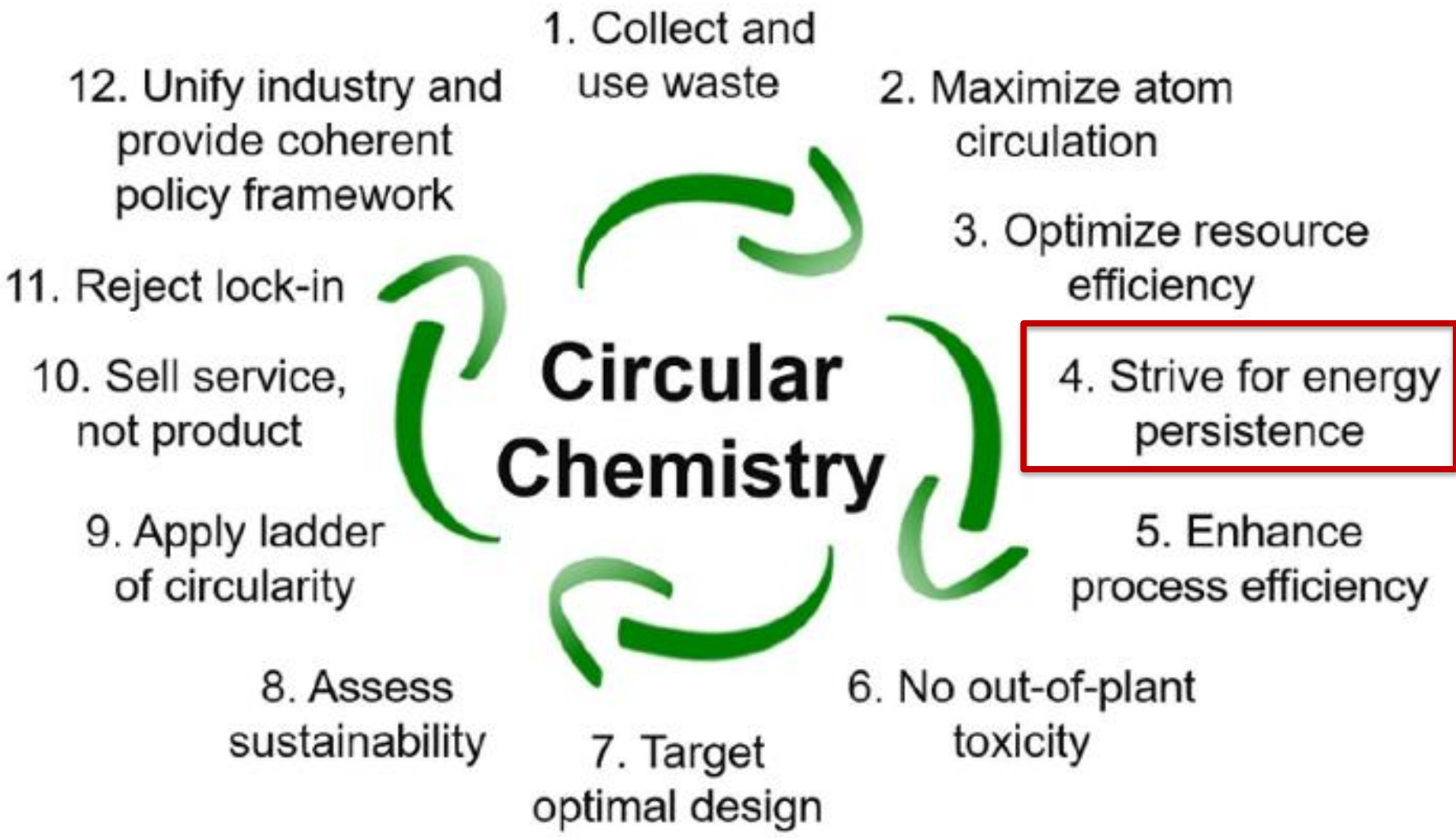
1. mining, efficient extraction and supply of inorganic raw materials, in particular critical raw materials (e.g. PMG, REE)

2. identification and selection of substitution materials for strategic applications (i.e. energy conversion and storage)

3. informed design of materials for circularity (also supported by Life Cycle Assessment and/or multiscale modelling)

4. recycling/recovery of inorganic materials, particularly, but not limited to, critical raw materials (e.g. rare earths, precious metals)

Examples of circular chemistry



Examples of circular chemistry applications

4. Strive for energy persistence

For repurposing waste material as a feedstock, it is important to realize recirculation of molecules and materials of the highest bond energy, thereby retaining as much of their renewable energy input as possible to maximize energy efficiency. By viewing the energy stored in materials/molecules as long-term investment, Circular Chemistry realizes conservation of energy and reduces additional energy inputs.

Examples of circular chemistry applications

4. Strive for energy persistence

Tire-Derived Material Feedstock

Tire-Derived Aggregate

Tire-derived aggregate is size reduced tires used to replace conventional light weight fill or other aggregates in a variety of civil engineering applications. It is defined in two types. Type “A” is comprised of shreds typically about 3 inches or smaller, and is used as drainage material, in septic systems, as vibration dampening layers under light rail tracks, and in landfill gas or leachate collection systems. Type “B” is comprised of shreds of 6-12 inches, and is typically used as light weight fill in embankments, behind retaining walls, or for road sections during slide repairs.

Ground Rubber

Ground rubber is made from whole tires, and is typically larger than 1/4- 3/4-inch in size, with up to 99.9 percent wire and fiber removed. Ground rubber is used in a variety of applications including loosefill playground surface nuggets, landscape covering and a variety of applications. Ground rubber is also used as equestrian arena surfacing.

Examples of circular chemistry applications

Tire-Derived Material Feedstock





Ground Rubber

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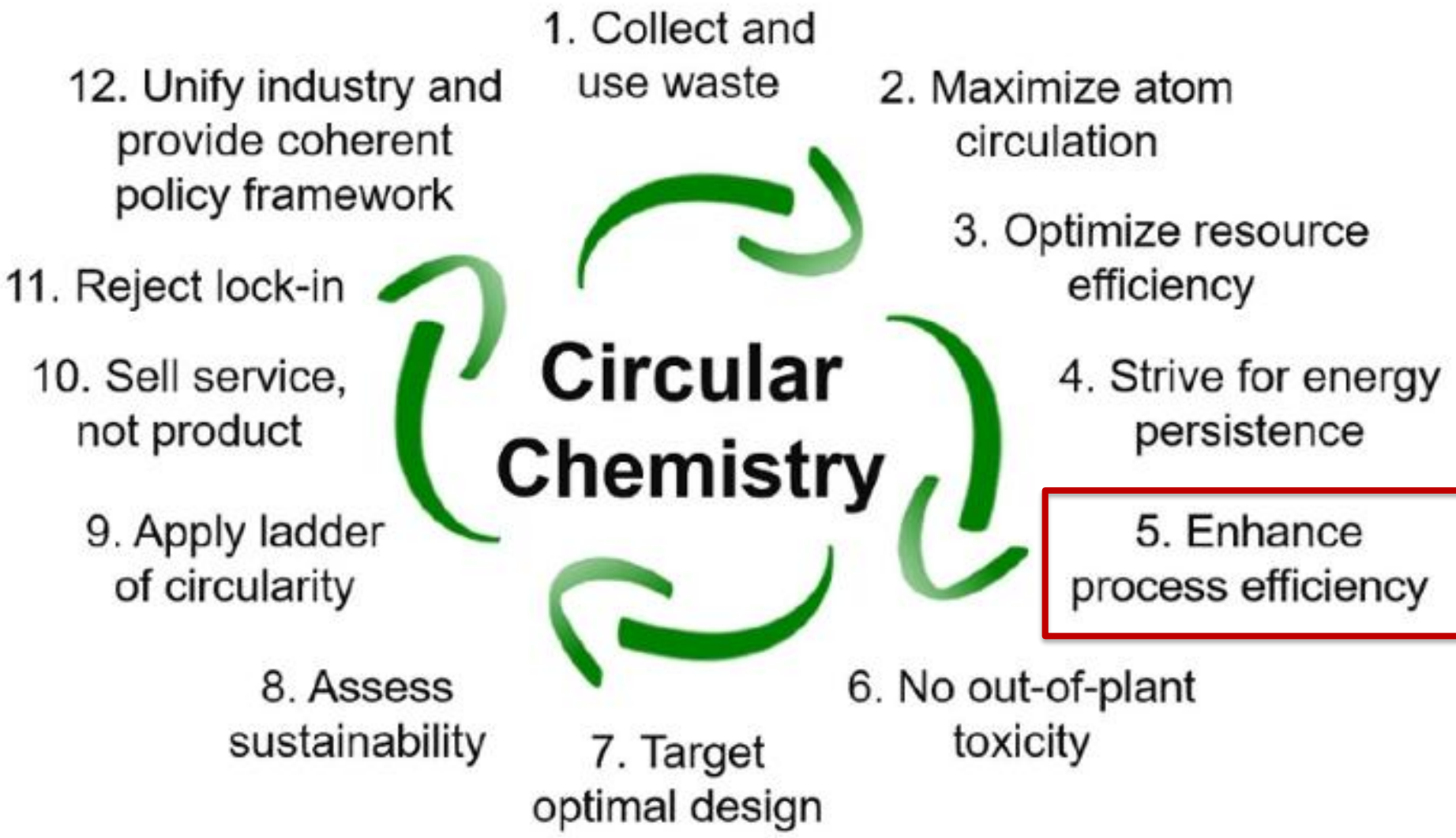
Examples of circular chemistry



Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

- process optimisation towards maximum yield (also supported by DoE)
- systematic variation of experimental parameters (also supported by DoE)
- optimisation of the whole process by Life Cycle Assessment (LCA)

Design of Experiment: a rational and still unexplored approach to inorganic materials synthesis, F. Lamberti, C. Mazzariol, F. Spolaore, R. Ceccato, L. Salmaso and S. Gross Sustainable Chemistry, 2022, , *3*(1), 114-130

In perspective (supported by A.I. and machine learning):

- materials genome
- materials discovery and mining

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

A chemical synthesis in solution: exploring the experimental parameters landscape

- pH
- solvent nature (viscosity, dielectric constant/polarity, density)
- chemical nature and structure of precursors (e.g. single source precursors, oligomerisation, decomposition paths)
- molar ratio among reagents
- nature and amount of additives (e.g. surfactant, structure directing agents, peptising agents, stabilising ligands etc.)
- ionic strenght
- time and temperature of processing
- flow and/or mixing conditions
- pressure
- further method-dependent specific conditions (e.g. sonication or microwave time and power, presence of confined space etc.)
- presence of unconventional reagents and/or conditions (e.g. ionic liquids, deep eutectic solvents, supercritical fluids, confined space etc.)

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

A chemical synthesis in solution: exploring the experimental parameters landscape: a more rational and less energy- and resources-consuming approach

Design of Experiment (R. Fischer, 1926)

statistical approach aiming at reducing the number of experiments while creating a mathematical model that predetermines the outcome of certain process variables modifications

simultaneously investigating the input variables (or factors, such as for example different reaction parameters) and the interactions between these factors, on the bases of the outputs (responses, or outcomes of the syntheses)

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

A chemical synthesis in solution: exploring the experimental parameters landscape: a more rational and less energy- and resources-consuming approach

WHY TO PERFORM DOE

- limited resources
- time to carry out experiment
- costs of required materials/equipment
- avoid reaching suboptimal settings
- avoid missing interesting parts of experimental region
- protection against external uncontrollable/undetectable influences
- getting precise estimates

key ideas

- change several factors simultaneously
- carefully choose which runs to perform
- use regression analysis to obtain effect estimates
- statistical software allows to
  - choose or construct designs
  - analyse experimental results

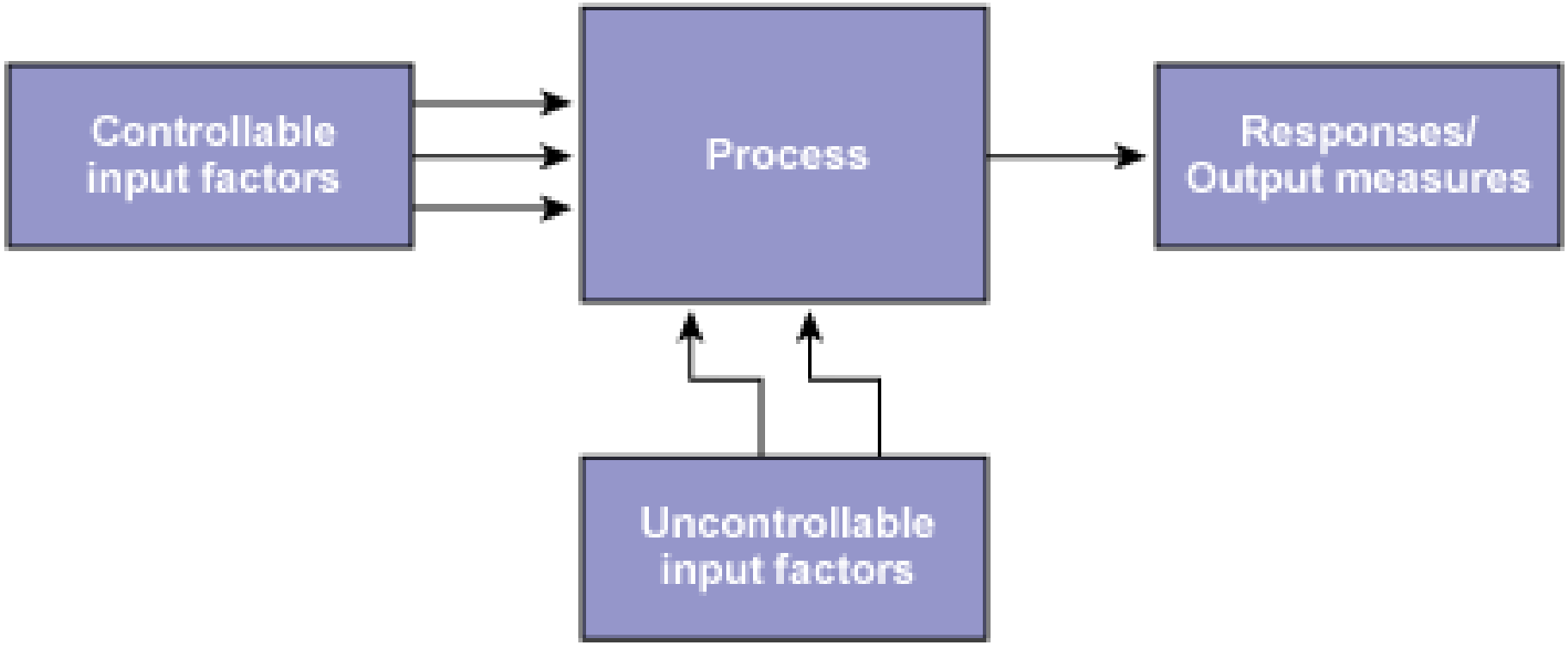
WHAT DOES DOE ENABLE

- improve process yield
- reduce variability
- reduce development time
- reduce overall costs

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

BASICS OF DOE



Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

BASICS OF DOE

- The advantage of applying DoE to chemical synthesis also lies in the possibility of assessing the synergistic effect of several parameters on the final result of the synthetic pathways, which would not be possible with a one-variable-at-a-time (OVAT) approach

- Design of Experiment approach will enable a rational planning of the synthetic efforts by careful screening the experimental parameters that most influence the final features, taking into account also interaction thereof, to identify the most promising combinations among them to obtain the desired product.

- Within this framework, in the field of chemical synthesis, the possibility to apply the DoE approach to figure out the relationship among the experimental parameters, the outcomes of the reaction and the final functional properties of the nanomaterials is extremely attractive as well as being an approach that can lead to a comprehensive exploration of the whole experimental factors

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency
BASICS OF DOE

Choice of a few qualitative categories or numeric values, called levels, of the controllable factors to be tested in the experiment. Responses and factors are then measured or controlled on a randomized sample of experimental units. Each combination of factor levels tested on this sample represents an experimental condition, also called treatment or run. The entire set of runs is the design and its choice is a fundamental part in DoE.

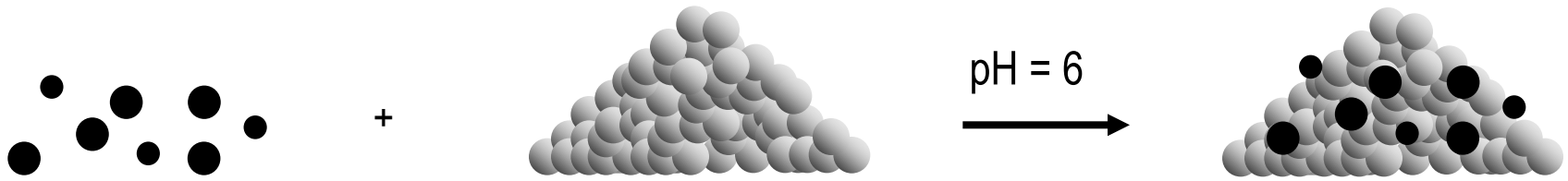
- Three basic principles of experimental designs:

1. randomisation: both the allocation of the experimental units to treatments and the order in which the individual runs are to be performed, are randomly determined;
2. blocking: a technique for dealing with known and controllable nuisance factors (i.e. factors having an impact on the response, but of no interest for the experimenter), blocking out their potential effect on the response;
3. replication: each factor combination is, generally, assigned to more than one experimental unit. Replicates are indeed multiple independent executions of the same experimental conditions which are processed individually in the experiment and should be run in random order. A replicate is not a repeated or duplicate measurement of the response variable which on the other hand is meant to reflect the inherent variability in the measurement system.

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

Phase i) Screening the reaction parameters

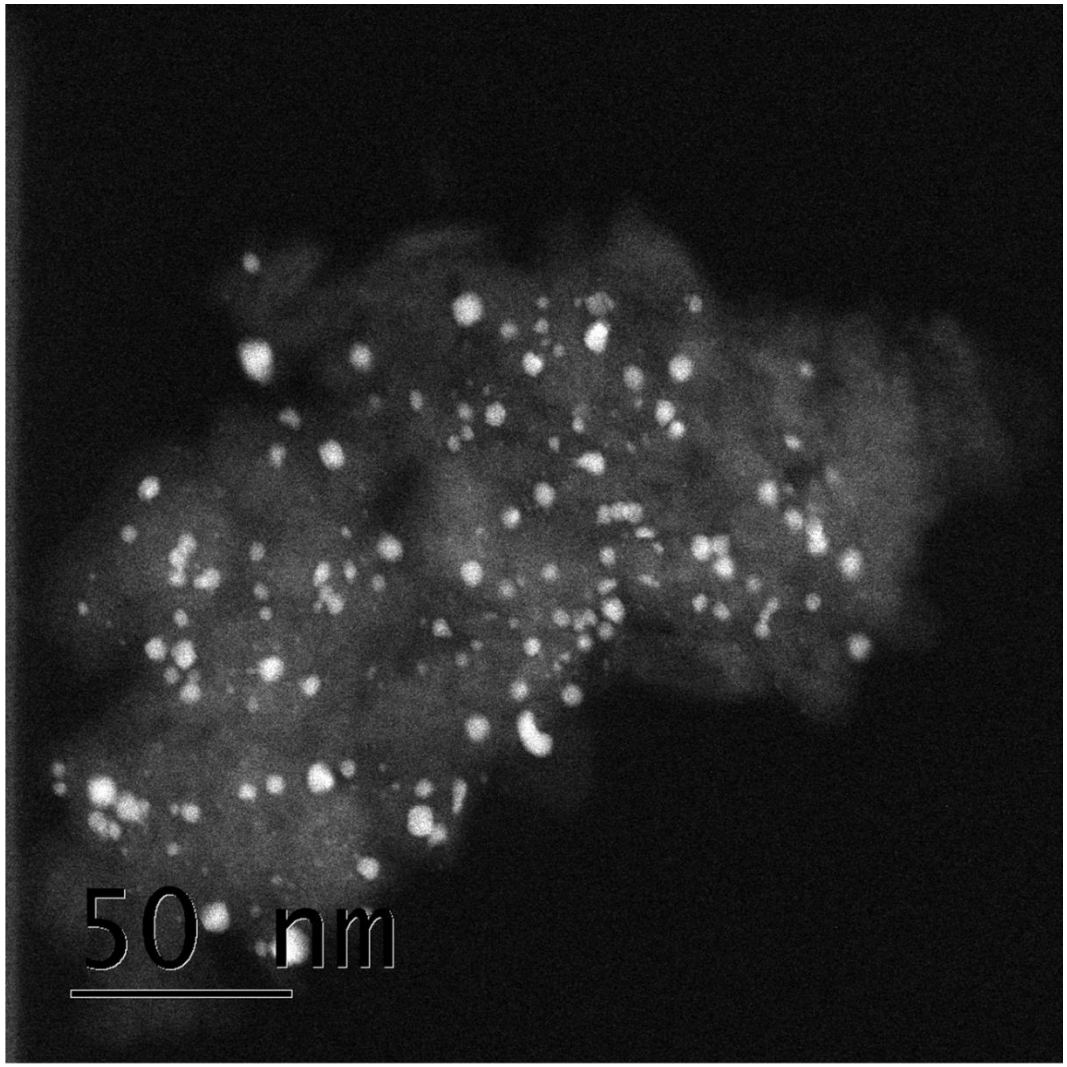


Tuning metal-support interactions (MSI)

- modified activity of the catalyst
- enhancing stability under operative conditions
- enhancing stability towards sintering

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency



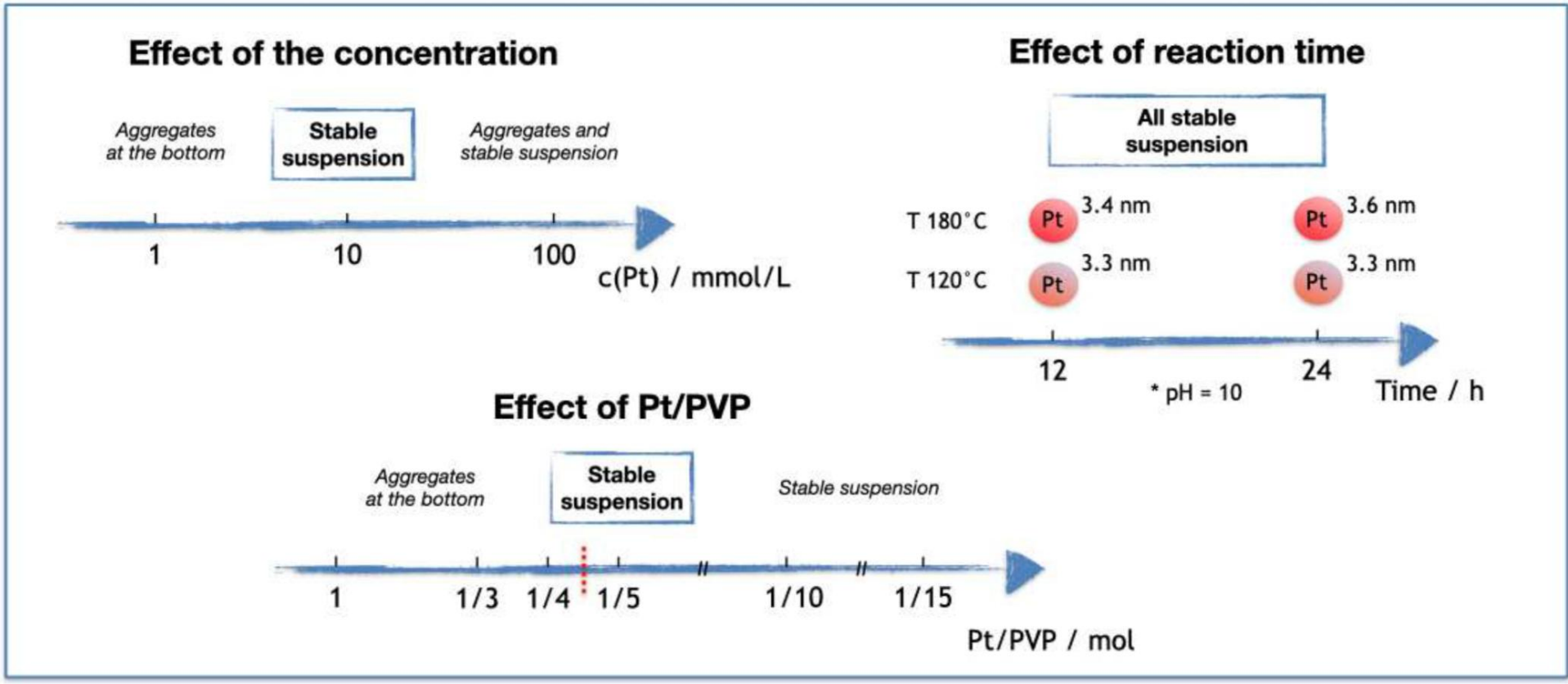
STEM-HAADF

Z-constrast: Intensity $\backsim Z^2$

$Z_{Pt} = 78$; $Z_{Al} = 13$

Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency
APPLICATION OF DOE



Examples of circular chemistry applications

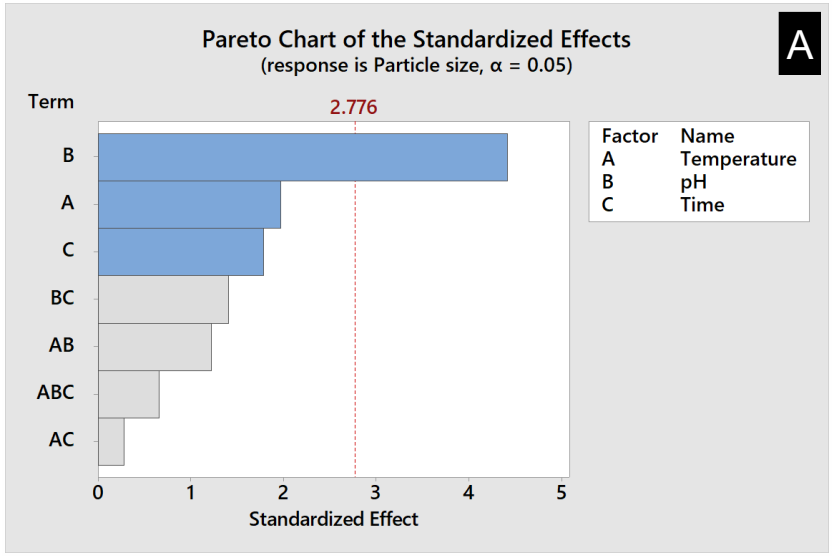
5. Enhance process efficiency & 3. Optimize resource efficiency

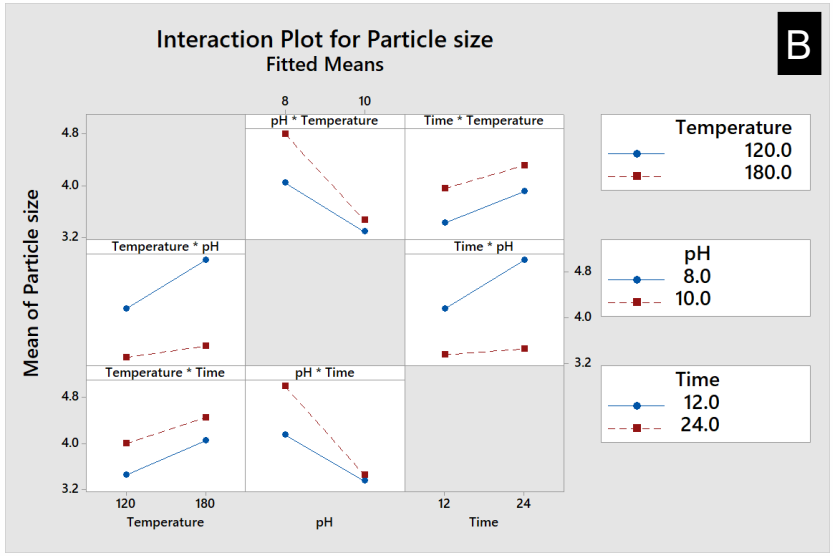
Phase ii) Planning and executing a DoE (2^3)
3 parameters (t, T, pH, 2 values: **full factorial design**

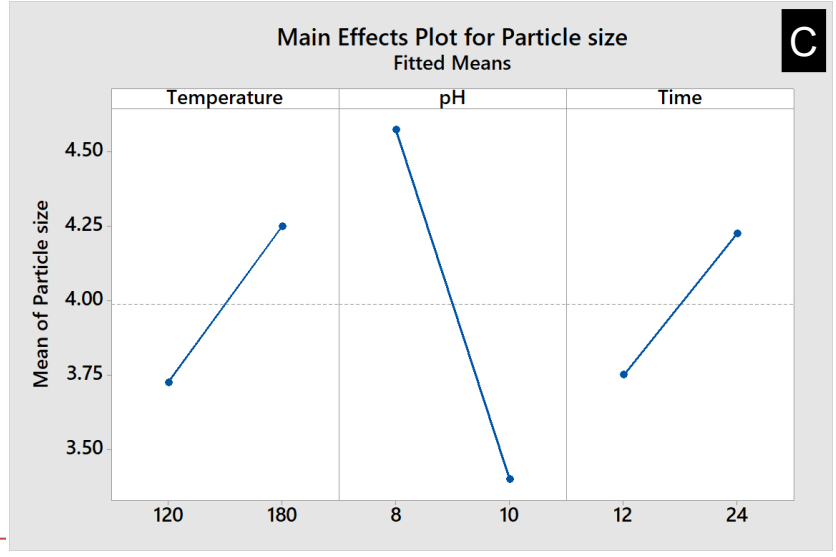
Name	Solvent	Precursor	Pt c [mM]	Stabilising agent	Pt/PVP [mol/mol]	Temperature [°C]	pH	Time [h]	Feret diameter [nm]	σ [nm]
HYD16	Water	Pt-TEAH	10	PVP	1/10	120	8	12	3.6	1.2
HYD17	Water	Pt-TEAH	10	PVP	1/10	120	8	24	4.7	2.0
HYD18	Water	Pt-TEAH	10	PVP	1/10	120	10	12	3.3	1.1
HYD19	Water	Pt-TEAH	10	PVP	1/10	120	10	24	3.3	1.0
HYD20	Water	Pt-TEAH	10	PVP	1/10	180	8	12	4.7	2.0
HYD21	Water	Pt-TEAH	10	PVP	1/10	180	8	24	5.3	2.3
HYD22	Water	Pt-TEAH	10	PVP	1/10	180	10	12	3.4	1.4
HYD23	Water	Pt-TEAH	10	PVP	1/10	180	10	24	3.6	1.6

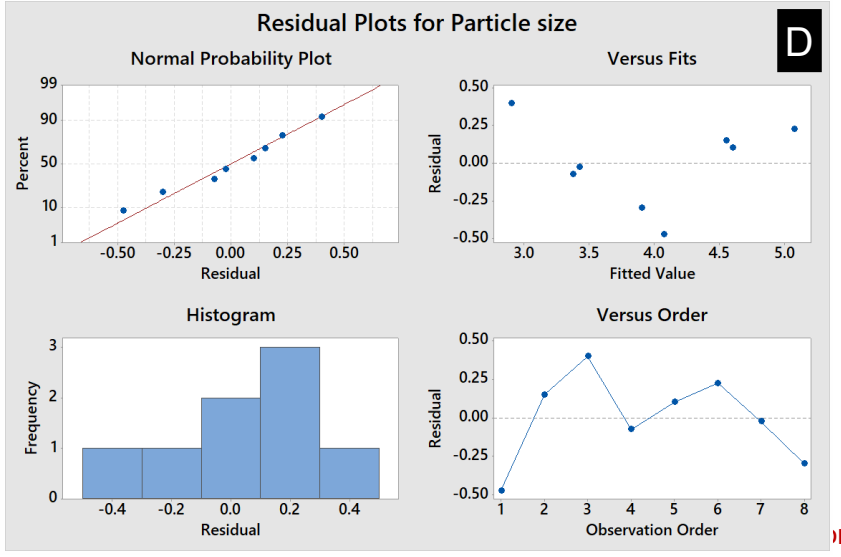
Examples of circular chemistry applications

5. Enhance process efficiency & 3. Optimize resource efficiency

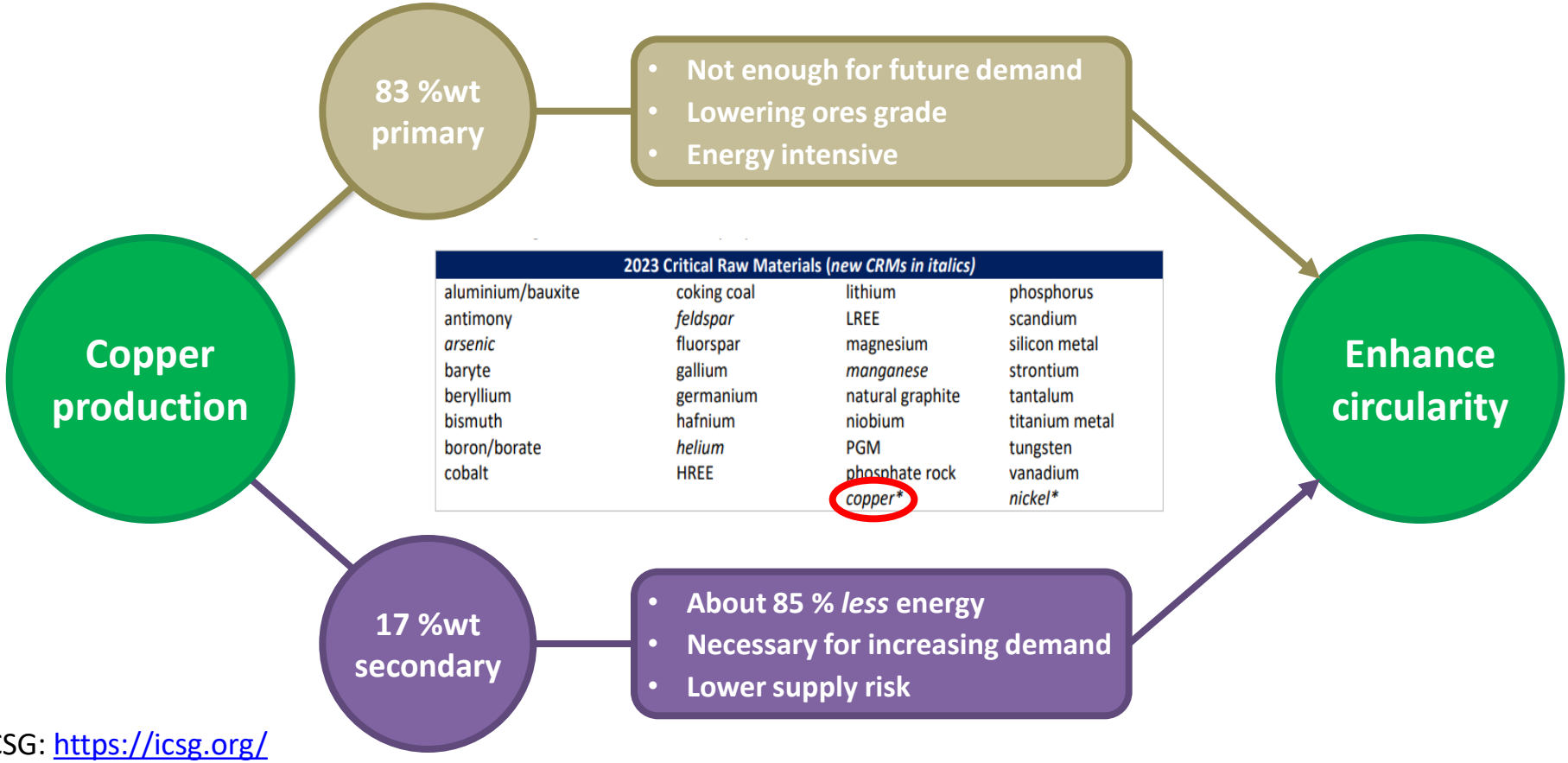








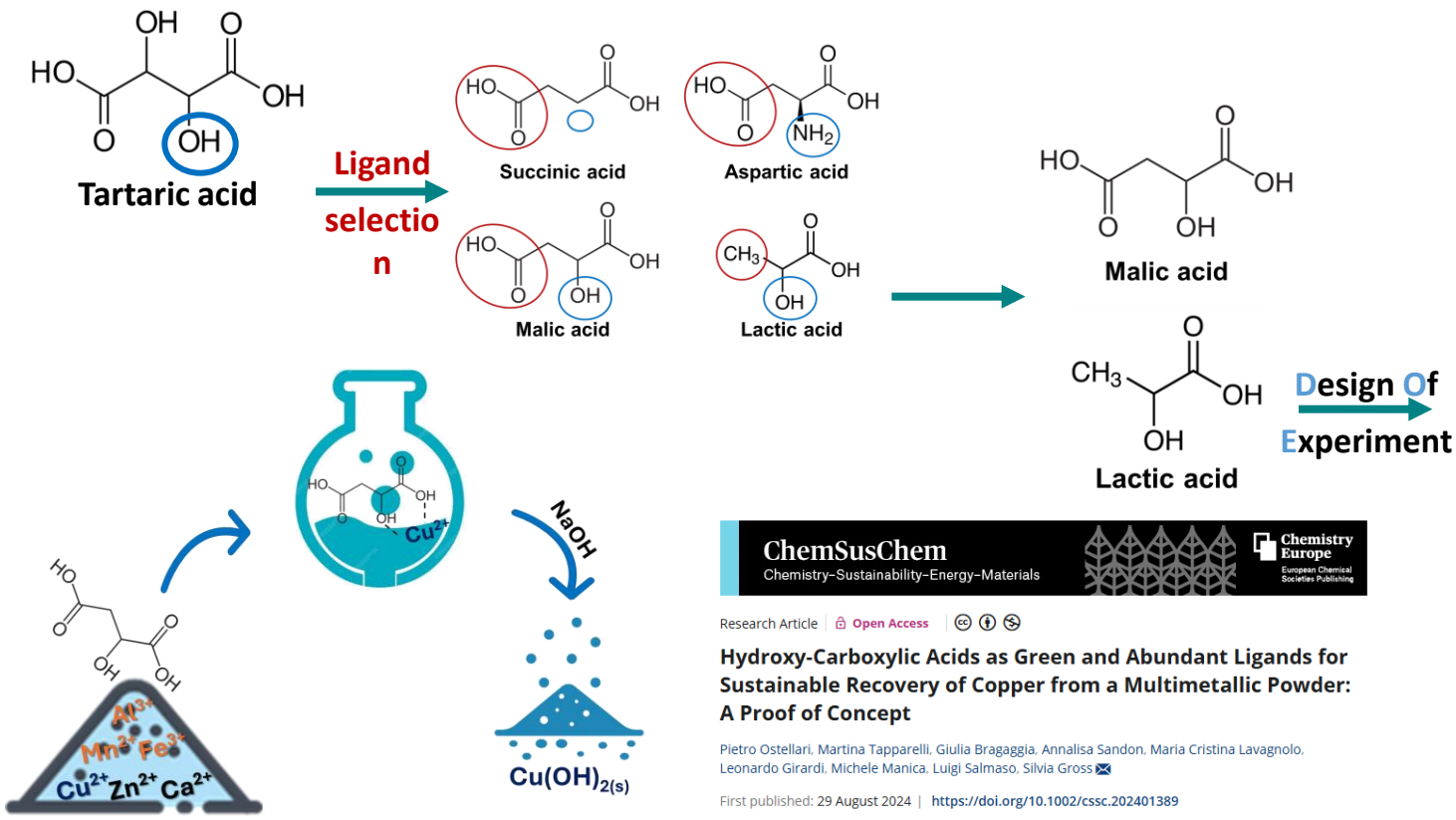
Examples of DoE applications



2023 Critical Raw Materials (*new CRMs in italics*)			
aluminium/bauxite	coking coal	lithium	phosphorus
antimony	*feldspar*	LREE	scandium
arsenic	fluorspar	magnesium	silicon metal
baryte	gallium	*manganese*	strontium
beryllium	germanium	natural graphite	tantalum
bismuth	hafnium	niobium	titanium metal
boron/borate	*helium*	PGM	tungsten
cobalt	HREE	phosphate rock	vanadium
		*copper**	*nickel**

ICSG: https://icsg.org/
Glob. Environ. Change, **39**, (2016), 305 - 315
European Copper Institute:
https://www.coppertransition.eu/

Examples of DoE applications



Optimized conditions	
Temperature	80 °C
pH	< $pK_{a,1}$ (≈ 2)
Cu/L (mol)	1:1
Time	1 h

ChemSusChem
Chemistry–Sustainability–Energy–Materials
Chemistry Europe
European Chemical Societies Publishing

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Hydroxy-Carboxylic Acids as Green and Abundant Ligands for Sustainable Recovery of Copper from a Multimetallic Powder: A Proof of Concept

Pietro Ostellari, Martina Tapparelli, Giulia Bragaggia, Annalisa Sandon, Maria Cristina Lavagnolo, Leonardo Girardi, Michele Manica, Luigi Salmaso, Silvia Gross

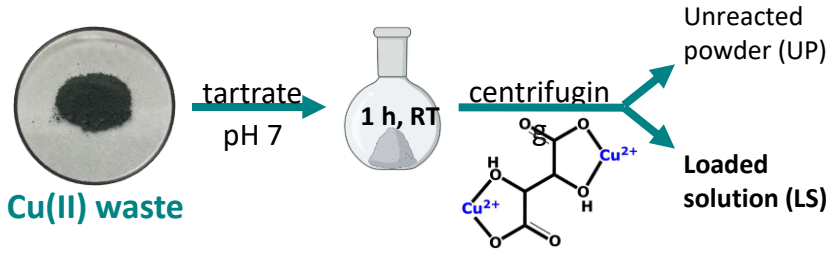
First published: 29 August 2024 | https://doi.org/10.1002/cssc.202401389

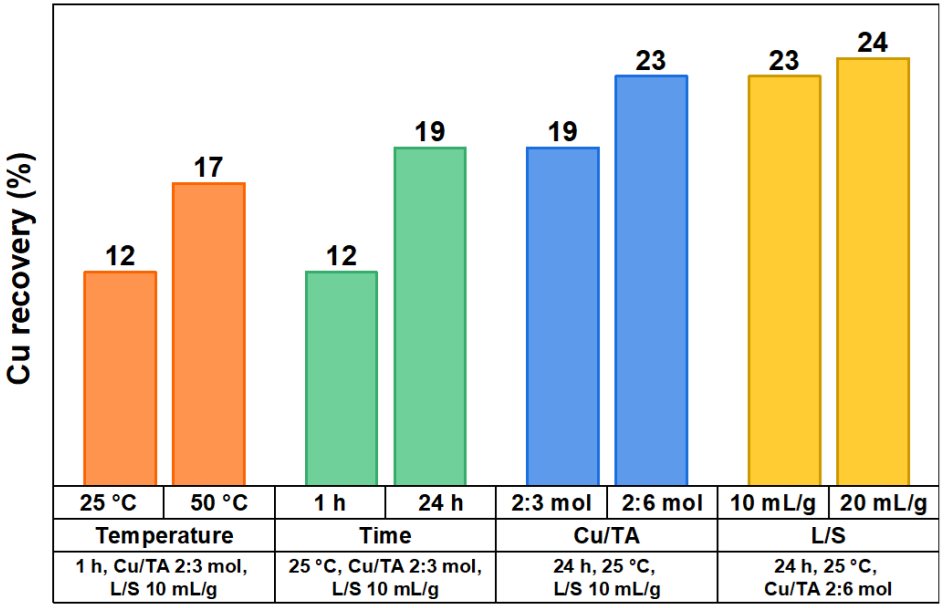
Published paper: *ChemSusChem*, **2024**, e202401389

Examples of DoE applications

Cu(II) industrial solid waste

- 32 %wt Cu
- **$Cu_2(OH)_2CO_3$** and **CuS**
- < 5 %wt Zn, Ca, Al, Fe
- Impurities of **Cd, Pb, Co, As**





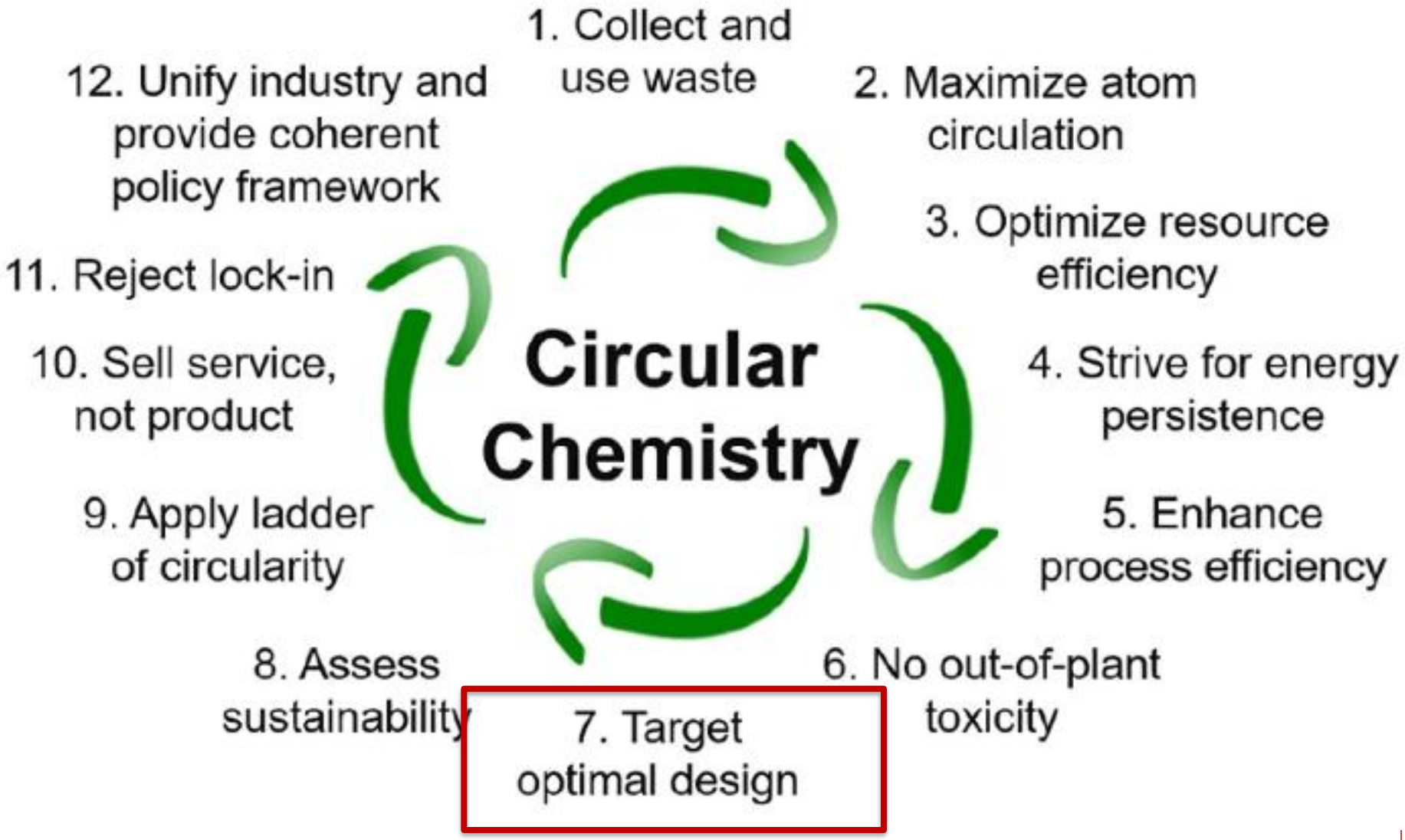
Varied parameters

- **Temperature:** from RT (25 °C) to 50 °C
- **Time:** from 1 h to 24 h
- **Cu/tartrate molar ratio:** from 2:3 to 2:6 mol
- **Liquid/Solid v/m ratio:** from 10 mL/g to 20 mL/g

- Zn, Ca, Al and Fe leached with Cu
- No **Cd, Pb, Co, As** in the **LS**

Ambient conditions

Examples of circular chemistry

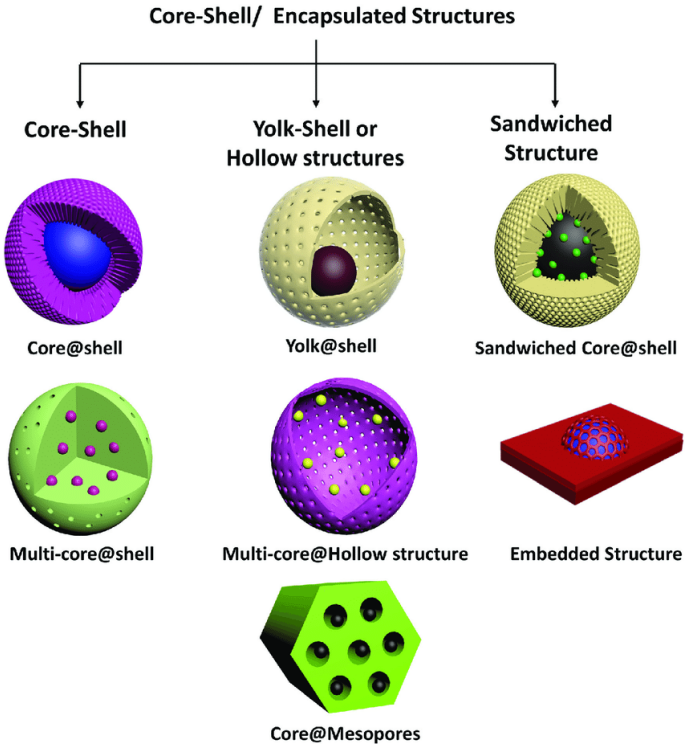


Examples of circular chemistry applications

Requirements down to the level of individual chemical substances for the downstream reuse and recyclability of consumer products

7. Target optimal design

- immobilisation of a catalyst allows it to be reused (heterogeneous catalyst)
- formation of core-shell structures (saving of PM)

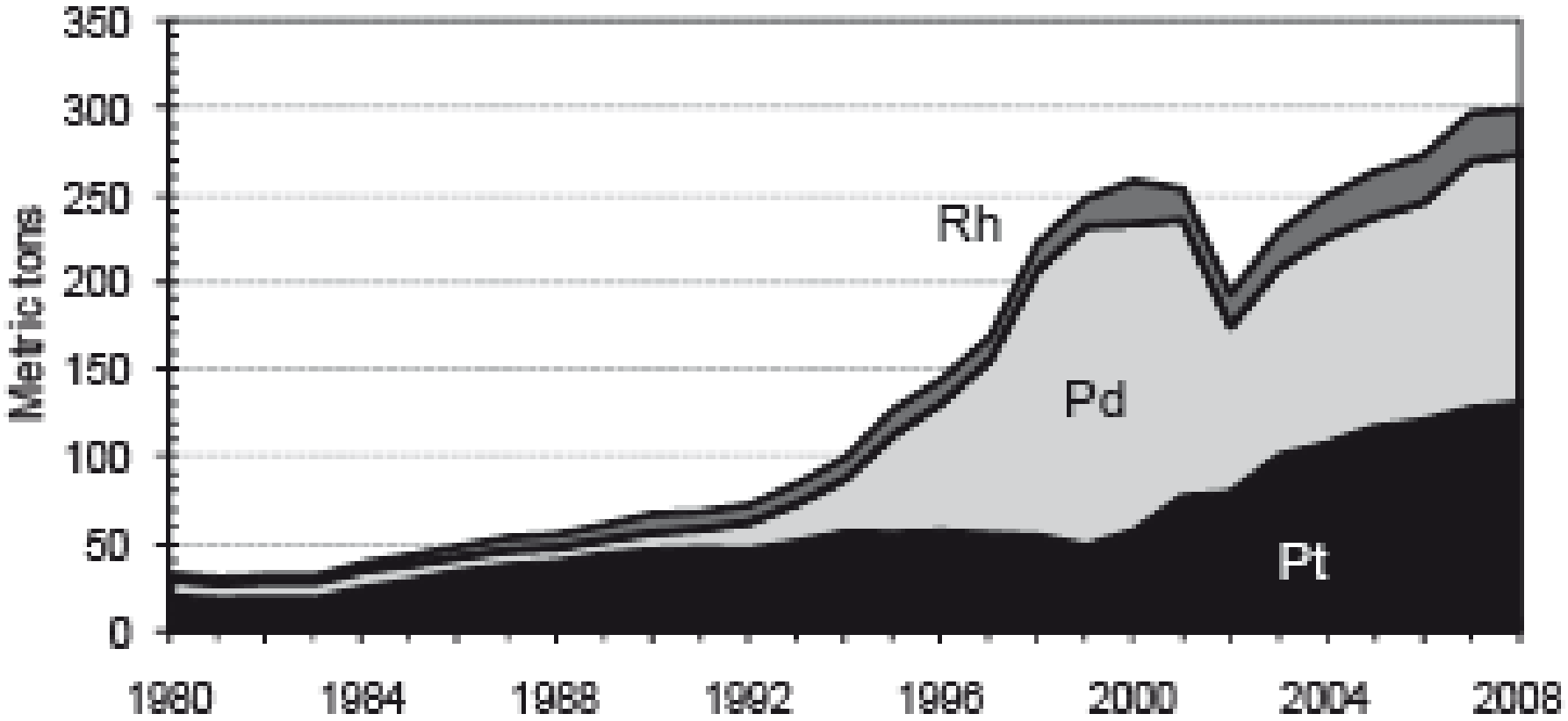


Source of the picture:

Das, Sonali & Pérez-Ramírez, Javier & Gong, Jinlong & Dewangan, Nikita & Hidajat, Kus & Gates, Bruce & Kawi, S.. (2020). Core–shell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO_2. Chemical Society Reviews. 49. 10.1039/C9CS00713J.

Examples of circular chemistry applications

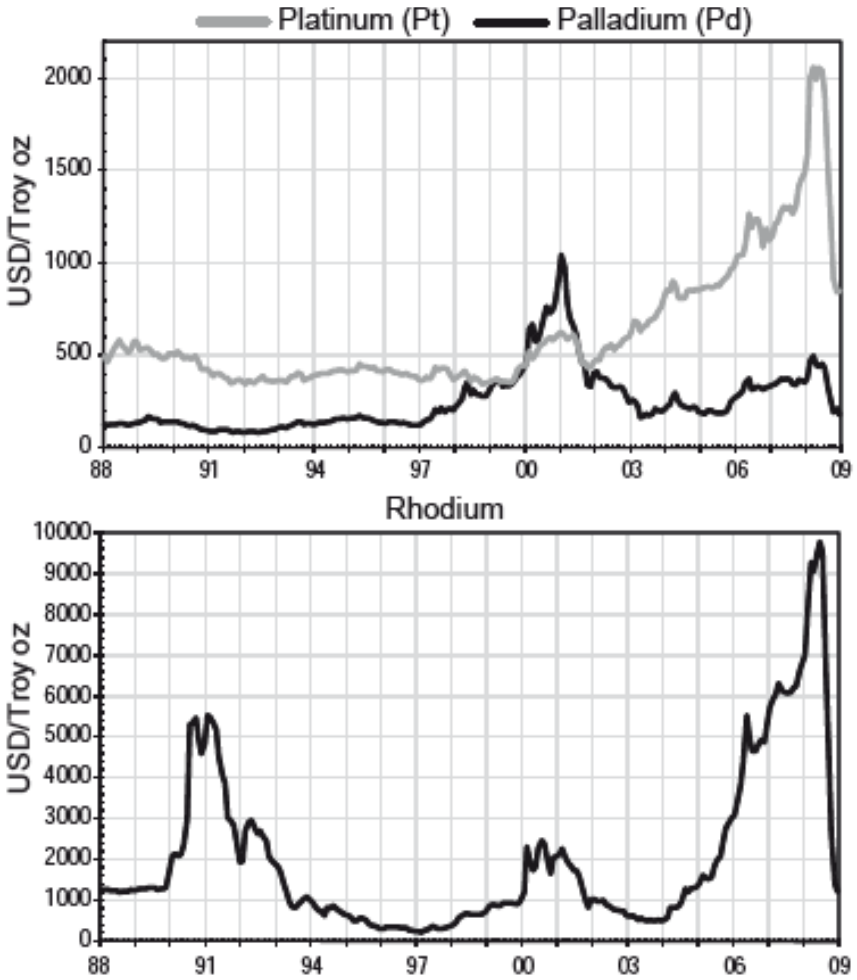
Avoid rebound effects



Global annual gross demands of platinum, palladium, and rhodium for use in car catalysts
C. Hagelüken and C. Meskers in *Complex Life Cycles of Precious and Special Metals*, MIT Press, 2010

Examples of circular chemistry applications

Avoid rebound effects

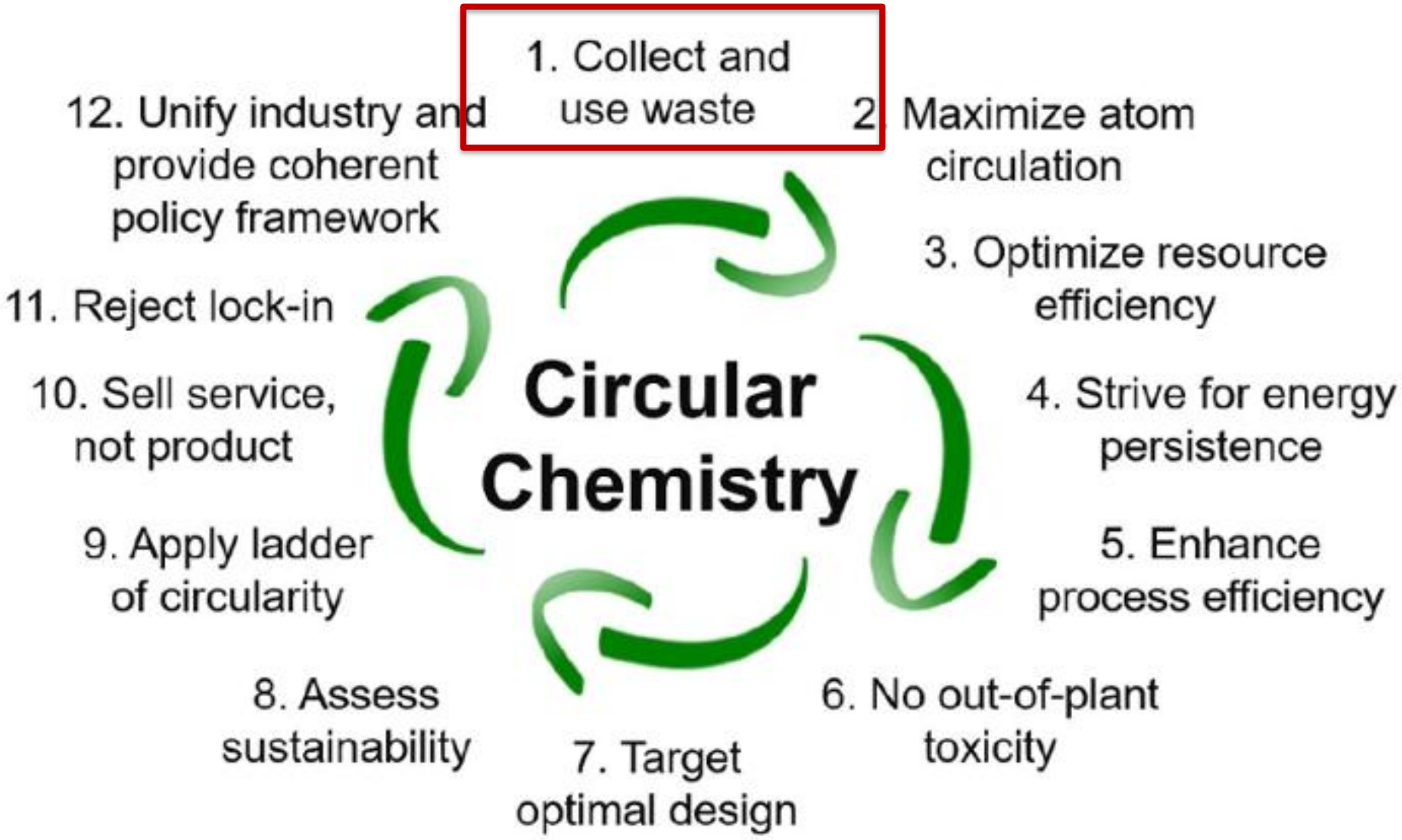


Price development for precious metals 1988-2009

Figure provided by Dr. C. Hagelücken, Umicore AG, Hanau, Germany

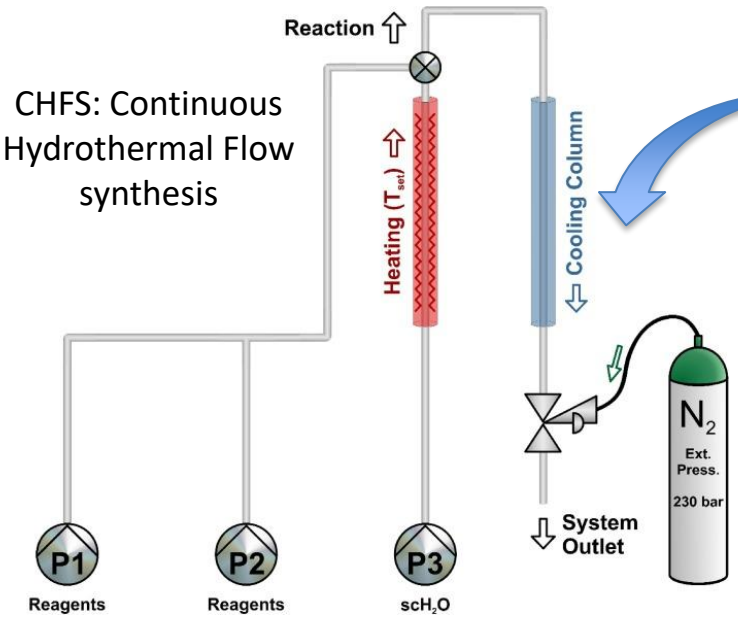
Replacements of any critical material should indeed start from the balance among the required functionality and the actual availability of materials, in order to avoid replacing one CRM with another: this is the "rebound effect"

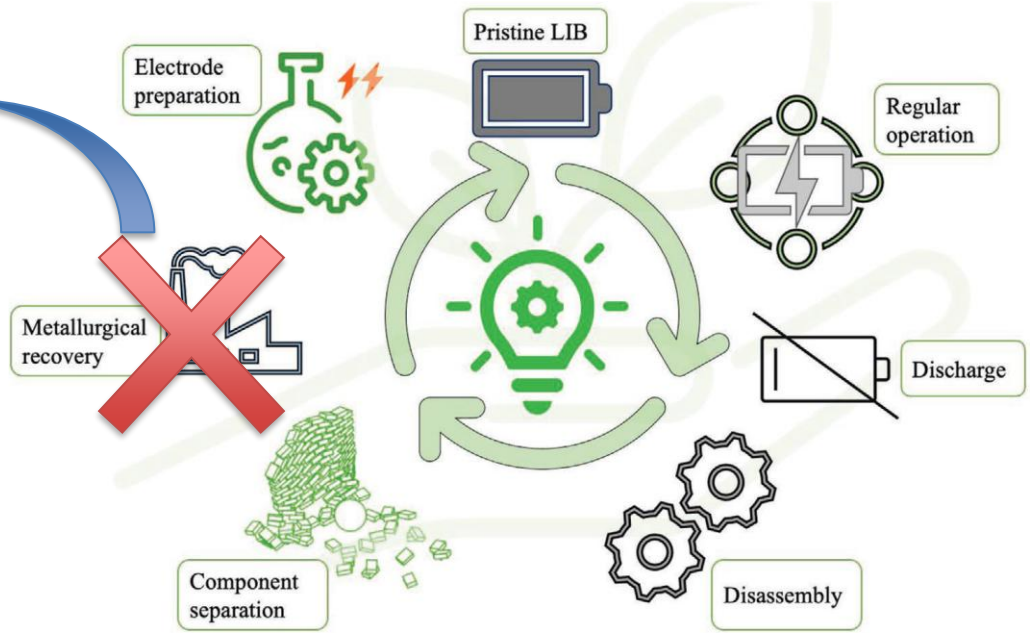
Examples of circular chemistry



CHFS for cathode regeneration in Li-ion Batteries

CHFS: Continuous Hydrothermal Flow synthesis





- ✓ Spent cathodes are regenerated synthetizing the corresponding oxides using the "black mass" (i.e. the cathode separated from the other battery component with impurities from the precedent step)
- ✓ Dissolved black mass (P1 and P2) reacts with supercritical (SC) water producing the oxides within seconds.
- ✓ Much less time and energy requires then classical solid-state synthesis methods
- ✓ Easy Up scalability (up to **ten kg/day**)
- × No metal selection is possible

PhD Project Federico Spolaore