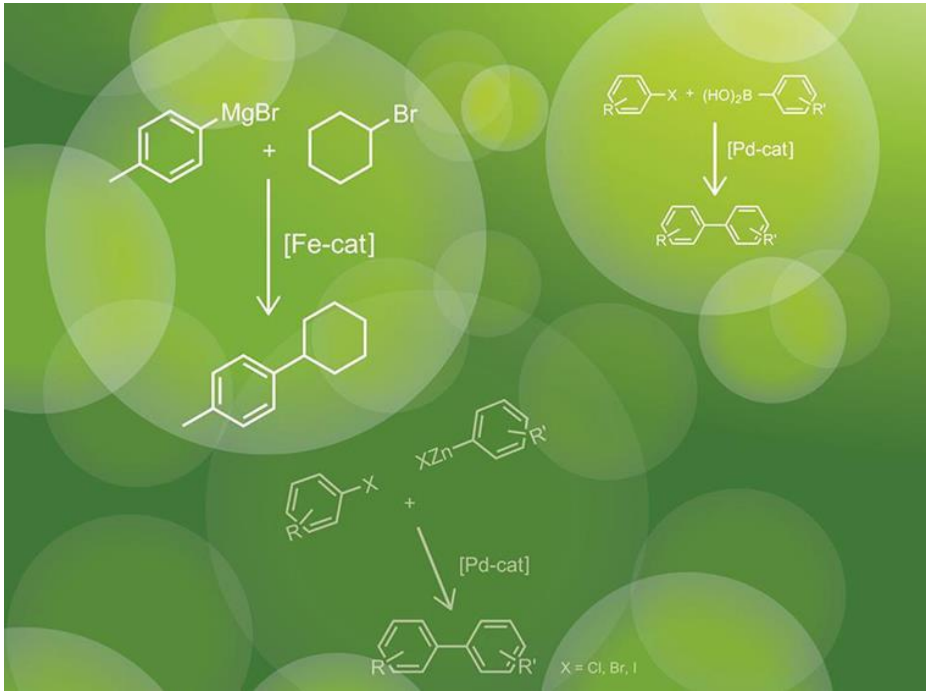
Aula de 27/09/2021

✓ Catálise, Química Verde e Sustentabilidade



https://sqquimica.com/quimica-verde-e-sustentabilidade/

nacoesunidas.org/pos2015/agenda2030/

NAÇÕES UNIDAS BRASIL

SOBRE A ONU FAÇA PARTE CAMPANHAS ONU NO BRASIL ESPECIAIS

17 OBJETIVOS PARA TRANSFORMAR NOSSO MUNDO DOCUMENTOS TEMÁTICOS A CÚPULA PRINCIPAIS FATOS AGENDA 2030 ODS1 ODS2 ODS3 ODS4 ODS5 ODS6 ODS7 ODS8 ODS9 ODS10 ODS11 ODS12 ODS13 ODS14 ODS15 ODS16 ODS17

Transformando Nosso Mundo: A Agenda 2030 para o Desenvolvimento Sustentável

Preâmbulo

Esta Agenda é um plano de ação para as pessoas, para o planeta e para a prosperidade. Ela também busca fortalecer a paz universal com mais liberdade. Reconhecemos que a erradicação da pobreza em todas as suas formas e dimensões, incluindo a pobreza extrema, é o maior desafio global e um requisito indispensável para o desenvolvimento sustentável.

Todos os países e todas as partes interessadas, atuando em parceria colaborativa, implementarão este plano. Estamos decididos a libertar a raça humana da tirania da pobreza e da penúria e a curar e proteger o nosso planeta. Estamos determinados a tomar as medidas ousadas e transformadoras que são urgentemente necessárias para direcionar o mundo para um caminho sustentável e resiliente. Ao embarcarmos nesta jornada coletiva, comprometemo-nos que ninguém seja deixado para trás.

Os 17 Objetivos de Desenvolvimento Sustentável e 169 metas que estamos anunciando hoje demonstram a escala e a ambição desta nova Agenda universal. Eles

pos2015/agenda2030/

OBJETIVOS DE DESENVOLVIMENTO SUSTENTÁVEL
17 OBJETIVOS PARA TRANSFORMAR NOSSO MUNDO

“Eles são integrados e indivisíveis, e equilibram as três dimensões do desenvolvimento sustentável:
a econômica,
a social e
a ambiental.”

Green Chemistry

PERSPECTIVE

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Sustainable chemistry: how to produce better and more from less?

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3.2. How can we define a sustainable product?

Defining the sustainability of a product is far from being easy because it is necessary to consider a complex set of parameters. It is important not to fall into the 'green' ideology or green washing and to keep in mind that above all, sustainable chemistry should be a vector of economic, societal and environmental progress across our planet. The 12 principles of green chemistry have been a catalyst for our society to enter the era of sustainability. Since 1998, chemistry has profoundly changed and we propose below an updated but non-exhaustive list of the ideal criteria a sustainable product, as well as resulting (eco-designed) mixtures, should fulfil (Fig. 3).

(1) The products should be non-toxic as regards ecosystems and humans and should be biodegradable or recyclable. The recyclability of molecules and materials is an important and fast-growing concept. In many areas and in particular that fossil carbon, chemistry should consider, from the outset of research, issues related to the end-of-life and recycling of molecules or materials.

(2) The products should be synthesised using a safe and environmentally-friendly process (saving atoms, water, metal, energy, greenhouse gases, *etc.*).

(3) The products must imperatively advance the intended application by integrating the challenges of global competitiveness (performance, safety, environmental impact, societal impact, *etc.*). The targeted products must therefore lead to a real scientific or technological breakthrough.

(4) There cannot be any projects regarding sustainable chemistry if there is no economic viability (in terms of investments, operating costs, *etc.*). Therefore, in addition to a low ecological footprint, sustainable chemistry should be able to turn a profit, that is to say produce both more and better at the same time.

(5) The products must be accepted by the consumer. Innovation in chemistry often involves research at the border of several disciplines in such a way that it results in groundbreaking innovations. Will the consumer accept these changes? And if so, how? The societal impact should be considered from the beginning of research. This directly implies the issue of education and major collaborative programmes are now appearing on the international scene. One may cite for instance (non-exhaustive list) educational actions from the Green Chemistry and Commerce Council (GC3),[27] the Global Network of Green Chemistry Centers (G2C2) in partnership with the Green Chemistry Network (GCN),[28] the Online Educational Resources for Green Chemistry & Engineering from the American Chemical Society,[29] the ACS Green Chemistry Institute,[30] *etc.*.

(6) The product should be preferably of renewable or recycled origin and supply chains should be sustainable. In the case of renewable carbon, chemistry has a duty to respect the food/non-food balance and to encourage virtuous agricultural practices. Indeed, with the human population increase on the planet, the area of arable land per inhabitant is continuously reducing and the pressure on agricultural resources and water is dramatically increasing. In order to avoid conflicts of use, it will be preferable to use non-food agricultural resources provided that they integrate the optimisation of land use in order to avoid them becoming nutritionally depleted. In the case of using recycled raw materials (notion of a circular economy) as a source of carbon, minerals, metals and energy, chemistry should take care not to destabilise the main channels of valorisation of these resources.

(7) The products must be marketed at a price which is in line with their application in such a way that the consumer can make both an economic and ecological choice.

(8) The products must have a noble use and must not harm humanity (chemical weapons, drugs, terrorism, *etc.*).

(9) In some cases, there are technical and environmental solutions but these can prove to be more costly. The additional cost should be borne either by the final market, namely the consumer, or by the manufacturer (reduced profits) or equally between the two. Public authorities should also have a part to play through aid policies (taxes, loans) or changes in regulation to favour the emergence of sustainable products.

(10) Chemistry is a dynamic system in the sense that the viability or sustainability of a chemical transformation depends directly on the cost of and access to competitive energy (oil, atom, coal, gas, solar, wind, *etc.*) and raw materials.[31] In the current conditions, it is clearly difficult to predict the sustainability of a process, a molecule or a material. A comprehensive life-cycle analysis gives us an accurate picture of the overall performance of a product in an application for a defined market.

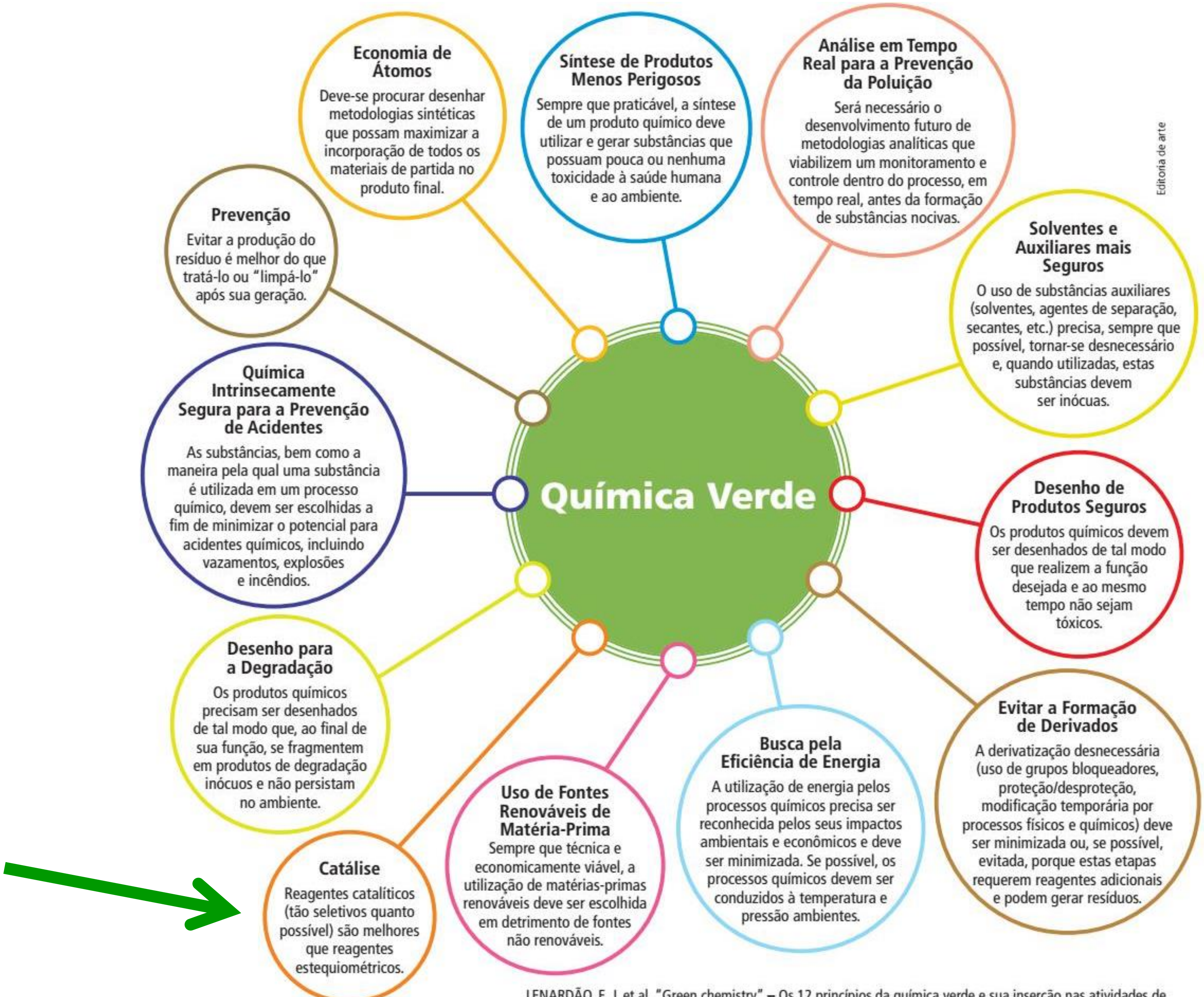
To conclude this section, it is important to never lose sight of the key objectives which are improving technical and application performance, economic efficiency and environmental and societal performances. A sustainable solution is a solution which provides a comprehensive benefit for a beneficial application at a societal level (wellbeing, preventing global warming, reducing the use of fossil carbon, *etc.*).

Few important criteria a sustainable product should fulfil.

A <u>QUÍMICA VERDE</u> pode ser definida como a utilização de <u>técnicas químicas e metodologias</u> que <u>reduzem ou eliminam</u> o uso de <u>solventes e reagentes</u> ou <u>geração</u> de <u>produtos e sub-produtos tóxicos</u>, que são <u>nocivos à saúde humana ou ao ambiente</u>.

12 princípios

http://www.funcap.ce.gov.br



LENARDÃO, E. J. et al. "Green chemistry" – Os 12 princípios da química verde e sua inserção nas atividades de ensino e pesquisa. **Química Nova**, v. 26 n.1, São Paulo, jan. 2003. Disponível em: <http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0100-40422003000100020>. Acesso em: 7 abr. 2016.

https://issuu.com/editoraftd/docs/quimica_1/233

1. Prevenção
É mais barato evitar a formação de resíduos tóxicos do que tratá-los depois que eles são produzidos;

2. Eficiência Atômica
As metodologias sintéticas devem ser desenvolvidas de modo a incorporar o maior número possível de átomos dos reagentes no produto final;

3. Síntese Segura
Deve-se desenvolver metodologias sintéticas que utilizam e geram substâncias com pouca ou nenhuma toxicidade à saúde humana e ao ambiente;

4. Desenvolvimento de Produtos Seguros
Deve-se buscar o desenvolvimento de produtos que após realizarem a função desejada, não causem danos ao ambiente;

5. Uso de Solventes e Auxiliares Seguros
A utilização de substâncias auxiliares como solventes, agentes de purificação e secantes precisa se evitada ao máximo; quando inevitável a sua utilização, estas substâncias devem ser inócuas ou facilmente reutilizadas;

6. Busca pela Eficiência de Energia
Os impactos ambientais e econômicos causados pela geração da energia utilizada em um processo químico precisam ser considerados. É necessário o desenvolvimento de processos que ocorram à temperatura e pressão ambientes;

7. Uso de Fontes de Matéria-Prima Renováveis
O uso de biomassa como matéria-prima deve ser priorizado no desenvolvimento de novas tecnologias e processos;

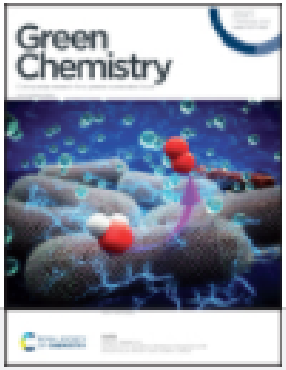
8. Evitar a Formação de Derivados
Processos que envolvem intermediários com grupos bloqueadores, proteção/desproteção, ou qualquer modificação temporária da molécula por processos físicos e/ou químicos devem ser evitados;

9. Catálise
O uso de catalisadores (tão seletivos quanto possível) deve ser escolhido em substituição aos reagentes estequiométricos;

10. Produtos Degradáveis
Os produtos químicos precisam ser projetados para a biocompatibilidade. Após sua utilização não deve permanecer no ambiente, degradando-se em produtos inócuos;

11. Análise em Tempo Real para a Prevenção da Poluição
O monitoramento e controle em tempo real, dentro do processo, deverá ser viabilizado. A possibilidade de formação de substâncias tóxicas deverá ser detectada antes de sua geração;

12. Química Intrinsecamente Segura para a Prevenção de Acidentes
A escolha das substâncias, bem como sua utilização em um processo químico, devem procurar a minimização do risco de acidentes, como vazamentos, incêndios e explosões.



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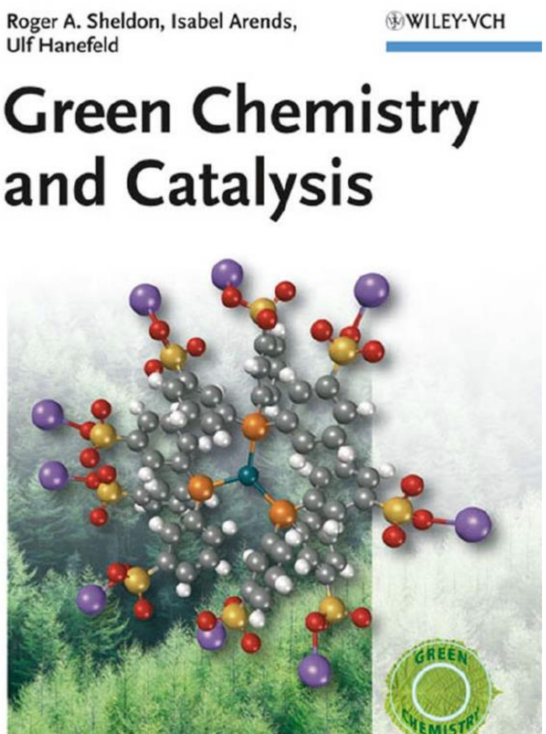

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E factors, green chemistry and catalysis: an odyssey

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Utilisation of biomass for sustainable fuels and chemicals: Molecules, methods and metrics

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Table 1.1 The E factor.

Industry segment	Product tonnage a)	kg waste b)/kg product
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–>50
Pharmaceuticals	10–10^3	25–>100

a) Typically represents annual production volume of a product at one site (lower end of range) or world-wide (upper end of range).

b) Defined as everything produced except the desired product (including all inorganic salts, solvent losses, etc.).

$$\text{E-factor} = \frac{\text{kgs of waste produced}}{\text{kgs of desired product}}$$

Industry sector	Annual production (tonnes)	Total waste (tonnes)	E-Factor
Oil refining	$10^6 - 10^8$	10^6	ca. 0.1
Bulk chemicals	$10^4 - 10^6$	10^5	< 1-5
Fine chemicals	$10^2 - 10^4$	10^4	5 - >50
Pharmaceuticals	$10 - 10^3$	10^3	25 - >100

Advantages:

- take into account solvent use

Disadvantages:

- what if large volumes of solvent are water, or if the waste consists of dilute aqueous solutions of benign inorganics?
- still concentrates on waste rather than other Green factors

https://slideplayer.com/slide/2400851/

The atom utilization [13–18], atom efficiency or atom economy concept, first introduced by Trost [21, 22], is an extremely useful tool for rapid evaluation of the amounts of waste that will be generated by alternative processes. It is calculated by dividing the molecular weight of the product by the sum total of the molecular weights of all substances formed in the stoichiometric equation for the reaction involved. For example, the atom efficiencies of stoichiometric (CrO_3) vs. catalytic (O_2) oxidation of a secondary alcohol to the corresponding ketone are compared in Fig. 1.1.

$$3\ PhCH(OH)CH_3 + 2\ CrO_3 + 3\ H_2SO_4 \longrightarrow 3\ PhCOCH_3 + Cr_2(SO_4)_3 + 6\ H_2O$$

$$\boxed{\text{atom efficiency} = 360 / 860 = 42\ \%}$$

$$Ph\ CH(OH)CH_3 + 1/2\ O_2 \xrightarrow{\text{catalyst}} Ph\ COCH_3 + H_2O$$

$$\boxed{\text{atom efficiency} = 120 / 138 = 87\ \%}$$

Fig. 1.1 Atom efficiency of stoichiometric vs. catalytic oxidation of an alcohol.

$$2\,CO + 3\,H_2 \longrightarrow HOCH_2CH_2OH$$

100% syn gas utilisation

$$2\,CO + 4\,H_2 \longrightarrow H_2C{=}CH_2 + 2H_2O$$

44% syn gas utilisation

Fig. 2 Syn gas utilisation.

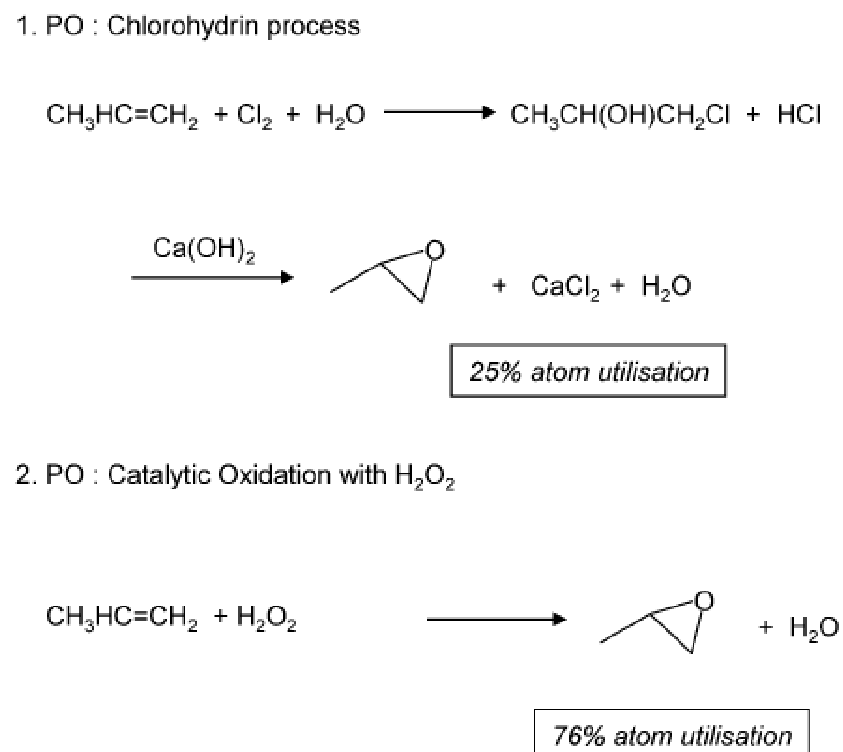
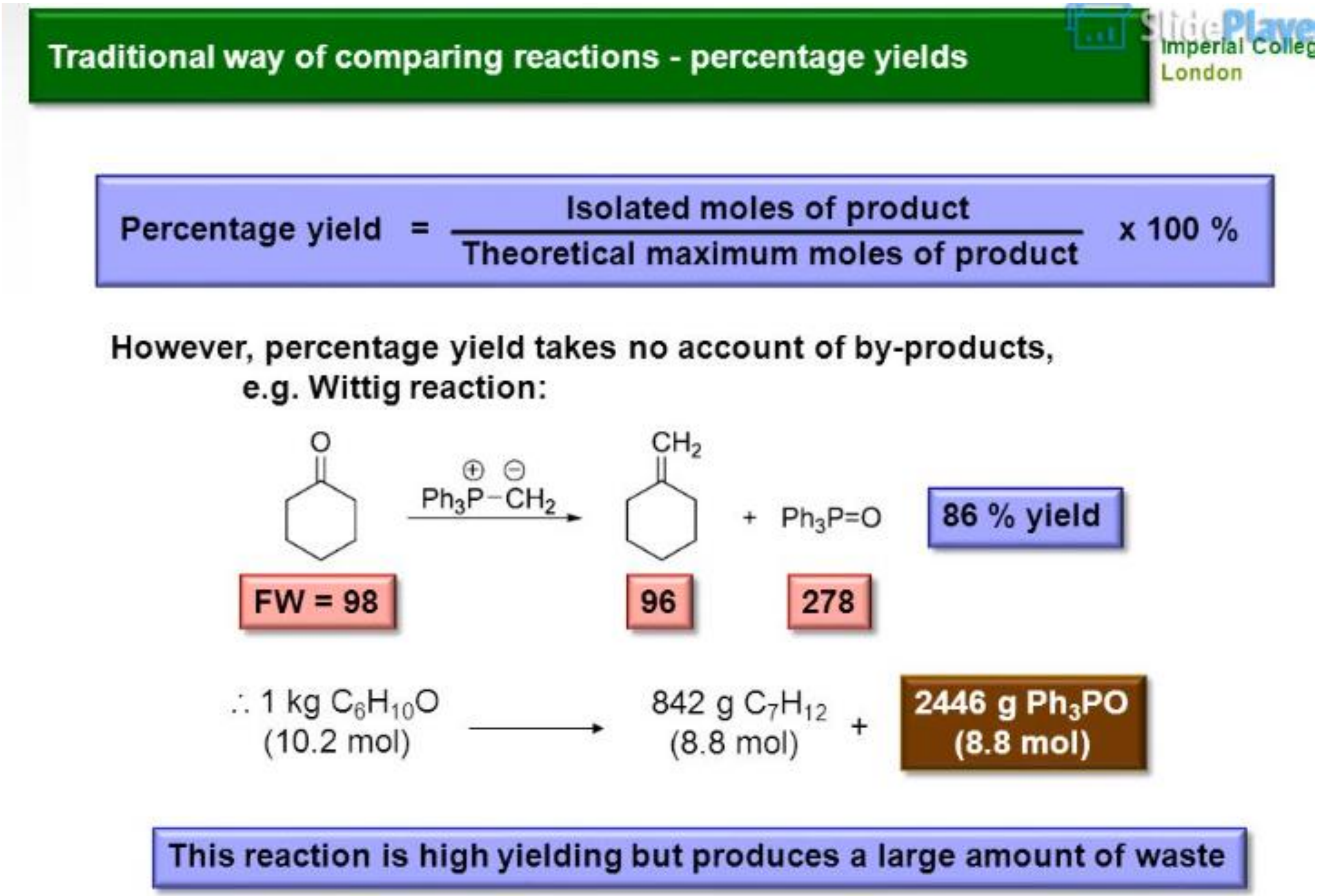


Fig. 3 Atom utilisation.



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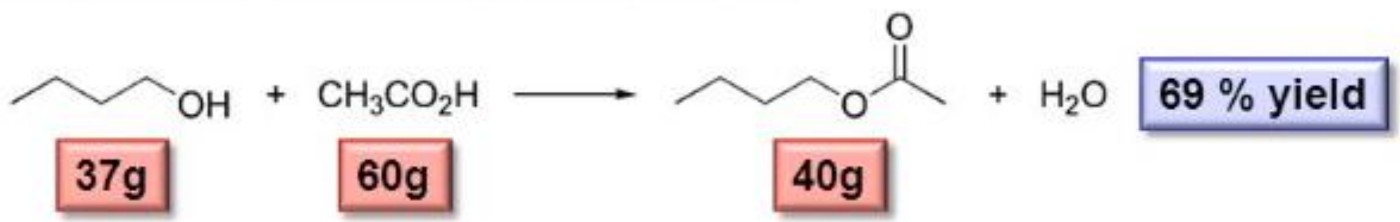
Effective Mass Yield - EMY

Imperial College London

$$EMY = \frac{\text{mass of desired product}}{\text{mass of non-benign reagents}} \times 100\ \%$$

e.g. esterification of n-butanol with acetic acid



EMY = (40 / 37) x 100 % = 108 %

The main disadvantage of this approach:
How do we judge if a reagent is non-benign?

e.g. esterification of n-butanol with acetic acid

Typical procedure: 37g butanol, 60 g glacial acetic acid and 3 drops of H_2SO_4 are mixed together. The reaction mixture is then poured into 250 cm^3 water. The organic layer is separated and washed again with water (100 cm^3), saturated $NaHCO_3$ (25 cm^3) and more water (25 cm^3). The crude ester is then dried over anhydrous Na_2SO_4 (5 g), and then distilled. Yield = 40 g (69 %).

Metric	Value	Greenness
yield	69 %	Moderate
atom economy	85 %	Good (byproduct is water)
E-factor	502 / 40 = 12.6	Moderate
EMY	40/37 x 100 = 108 %	Very good

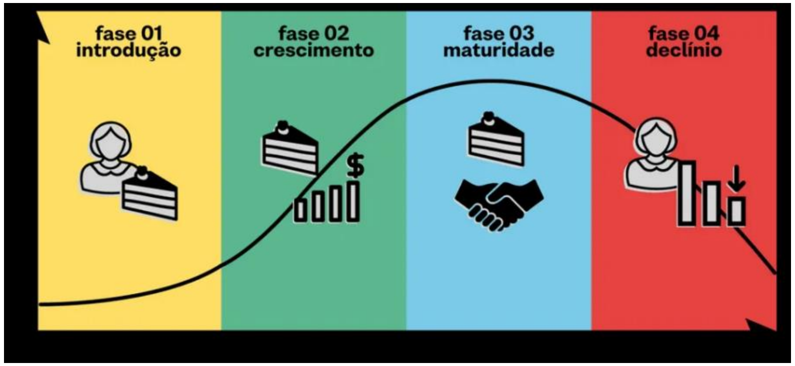
EMY indicates that this reaction is very 'green'

https://slideplayer.com/slide/2400851/

Instead, when questioning the sustainability of competing chemical reactions we tend to compare the nature of five individual components:

- raw materials
- reaction types (e.g. additions, eliminations etc)
- reagents (e.g. catalysts)
- reaction conditions (including solvents)
- toxicity of products (including waste by-products)

The only complete answer comes from a life cycle analysis



https://www.friendslab.co/o-que-e-ciclo-de-vida-do-produto

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	Natural Abundance (ppm)	Supply Risk Index[1]	Carbon Footprint (Kg CO_2e)	Water withdrawal required to extract 1 Kg Metal
Pd	0.015	7.6	10,223[2]	508,000 L
Ni	90	6.2	10.93	390 L
Cu	68	5.2	1.8-5.1	79 L
Fe	56,300	4.3	1.5	16-23 L

1. British Geological Association http://www.bgs.ac.uk/mineralsuk/statistics/riskList.html
2. Average of Figures for Russia and South Africa

https://www.bgs.ac.uk/mineralsuk/statistics/riskList.html

A pegada de carbono (carbon footprint - em inglês) é uma metodologia criada para medir as emissões de gases estufa. As mesmas, independente do tipo de gás emitido, são convertidas em carbono equivalente. Esses gases são emitidos na atmosfera durante o ciclo de vida de um produto, de processos ou de serviços.

https://www.ecycle.com.br/3874-pegada-carbono.html#:~:text=A%20pegada%20de%20carbono%20(carbon,de%20processos%20ou%20de%20servi%C3%A7os.

https://youtu.be/dCW-SoULW6A

	Aula 3
	Industrial Catalysis: A Practical Approach, Second Edition. Jens Hagen **Cap 10) Environmental Catalysis and Green Chemistry**
	Exercício 10.0 Qual são as maiores fontes de poluição do ar e a importância de estudos para controla-las? Quais as áreas abordadas pelo capítulo em estudo?
	Exercise 10.1 Why is the automotive exhaust catalyst called a three-way catalyst?
	Exercise 10.2 Which metals are used in the automotive catalyst and what reactions do they catalyze?
	Exercise 10.3 What are the major compounds of exhaust gases?
	Exercise 10.4 Describe how NOx can be removed from the exhaust when a car operates under lean-burn conditions (i. e. oxygen rich). Why is it attractive to drive cars under lean-burn conditions?
	Exercise 10.5 Explain the common characteristics of the NSR catalytic system for NOx abatement based on the principle „oxidation before reduction“ employing the oxidation states of all stages.
	Exercise 10.6 A BASF process proceeds according to the following equation:
	$4NO + 4NH_3 + O_2 => 4N_2 + 6H_2O$
	a) What is the significance of the process and what is it called?
	b) Catalysts and temperature range?
	Exercise 10.7 You can select a suitable catalyst for a catalytic afterburning process from monoliths or pellets. Which process parameters are mainly influenced by your choice?
	Exercise 10.8 Explain the atom efficiency concept by comparing the classical chlorohydrin route and the newer petrochemical ethylene oxide manufacture.
	Exercise 10.9 What is an *E*-factor? Which processes usually have the highest *E*-factors?
	Exercise 10.10 In the nitration of aromatic compounds, solid acid catalysts such as clays and zeolites are an alternative to the conventional process employing a mixture of HNO_3/H_2SO_4. List some reasons in view of green chemistry.
	Exercise 10.11 Which advantages for process development can be offered by ionic liquids?