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Green Chemistry and Sustainability of Chemical Safety and Security

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Abstract:

According to the twelve principals of eco-friendly modern science which names "Green Chemistry" along with their practical environmental metrics which necessary to be used in order to develop, achieve, and perform the sustainability of the chemical safety and security, through an application of these practical metrics in both of academia and industry.

These metrics are includes: e-Factor, Atom Economy, Atom Efficiency, Effective Mass Yield, Carbon Efficiency, Reaction Mass Efficiency, and Environmental Quotient. While, there are many issues not addressed by these metrics such as energy concerns (Process–interior and exterior), life cycle analysis, renewable feedstock (starting materials), reaction types (safety or stoichiometric vs. catalysts reagents), and environmental quotient as well.

However, the practical metrics and measurements have been discussed separately.

Keywords:

Green chemistry, Twelve principles, Metrics, Sustainability development, Chemical safety and security.

Introduction:

Green chemistry is the technique of industrial processes for chemical reactions characterized by energy efficiency, reduce, or preferably prevent the formation of waste materials or unwanted side-products, avoid the use of reagents or dangerous toxic solvents as much as possible, the use of renewable raw materials, the use of (reusable) solid heterogeneous catalysts, recycling of both formed products and by-products in order to achieve the principle of sustainability (sufficiency of the needs of current generations without the consumption of raw materials, including subsequent generations requirements in the future).[1]

The scope of the green chemistry is to make chemical reactions safe, harmless, friendly to humans and the environment, more efficient and cleaner, through the application of the principles of twelve green chemistry concerned with reducing or preventing the use or generation of hazardous toxic materials at the design, manufacturing, and the application of chemicals; Replace toxic reagents with renewed safe reagents; Reduce or prevent the generation of products and toxic side as well as the rationalization of energy consumption. Avoid using solvents as possible (at least using the benign solvents such as water) ; Taking into account the time of the analysis in the detection of results (development of analytical techniques) before for pollution; Use of factors usable many times and recycling of solid assistance through revitalized to get high selectivity and product, as well as the use of renewable raw materials; When the design, adoption of the involvement of all materials used in the chemical reaction for the purpose of producing the required final article (atomic economy).

There are some of the factors and basic principles of green chemistry (metrics of environmental efficiency):[2]

Atom Economy, this is understood as a tool for the design of chemical reactions which refers to the number of atoms of the reactants actually involved in the formation of the desired product and how many involved in the side-products or how much of the reactants remain in the final product:

$$\%\ \text{Atom Economy} = 100 \times \frac{\text{Molar mass of product}}{\text{Molar masses of reactants}} \qquad (1)$$

$$\text{Yield} = \frac{\text{Actual quantity of products achieved}}{\text{Theoretical quantity of products achievable}} \times 100\% \qquad (2)$$

$$\text{Selectivity} = \frac{\text{Yield of desired product}}{\text{Amount of substrate converted}} \times 100\% \qquad (3)$$

The real benefit of this concept is the possibility of its account in the planning stage of the chemical reaction equation, and similarly also to the efficiency calculations of the chemical reaction in terms of yield) and the selectivity.

Atom Efficiency, this concept can be used instead of atom economy and the yield:

$$\textbf{Atom Efficiency} = \textbf{\%Yield} \times \textbf{Atom Economy} \qquad \textbf{(4)}$$

It should also be high values for the purpose of obtaining a green chemical reaction (atom economy could be 100% and yield 10% making that a not very green reaction).

E-Factor, this term can be defined as the ratio of the amount of waste (Kg) to the required product (Kg), and it directly refers to solvents minimization:

$$\textbf{E-Factor} = \frac{\textbf{Raw materials (total input)-Product}}{\textbf{Product}} \qquad \textbf{(5)}$$

This tool is very useful for industry where it show the magnitude of waste problem (organic waste and aqueous waste) that accompaniment to produce any required material, or in other words, enter into its calculations all the used materials in the reaction from start to finish, including that the used water in the washing and purification processes to separate the product, and therefore, the consumption of significant amounts of the benign waste (such as water, alcohol diluted with ethanol, acetic acid, and low-lying concentrations of inorganic salts moderate) makes environmental impact seems worse than it really is.

Reaction Mass Efficiency, this metric equal to the ratio between the mass of desired product and the masses of all used reactants (percentage of the mass of the of the reactants that remain in the product) which it takes into account the atom economy, yield, and reactant stoichiometry.

$$\textbf{RME} = \frac{\textbf{Product (Kg)}}{\textbf{All used reactants (Kg)}} \times \textbf{100\%} \qquad \textbf{(6)}$$

Effective Mass Yield (EMY), this metric is found to exceed the problem of calculating the benign wastes in accounts of E-factor.

$$\textbf{EMY} = \frac{\textbf{Product (Kg)}}{\textbf{Hazardous (non-benign) reagents (Kg)}} \times \textbf{100\%} \qquad \textbf{(7)}$$

This metric ignores the **RME** factor because the issue related with existence possibility of benign and/or non-benign solvents in the chemical reaction.

It is approaching to be a reciprocal proportion to the value of the E-factor, but it does not enter into its calculations the benign materials such as water and diluted ethanol (it is the ratio between the mass of desired product to the mass of all non benign used materials). This concept may be used again abused because there is no agreed consensus on what constants governing on the benign materials to be neglected or recognized in metrics of environmental efficiency.

Carbon Efficiency, this equal to the ratio between the mass of carbon in product and the mass of carbon in reactants (mass of carbon equal to the number of moles by carbons of each material). This metric takes into account the yield and stoichiometry and also is important and useful tool because its directly related to greenhouse gasses (CO_2 emissions).[3]

$$\textbf{Carbon Efficiency} = \frac{\textbf{Mass of Carbon in Product}}{\textbf{Mass of Carbon in reactants}} \times \textbf{100\%} \qquad \textbf{(8)}$$

Environmental Quotient (EQ), It is multiplied by the environmental factor (E-factor) with side-products of dangerous non-friendly factor (Q-factor):

$$\textbf{EQ = E-Factor} \times \textbf{Q-Factor} \qquad \textbf{(9)}$$

So, that could Q amount is equal to (100) of salts of heavy element or of (1) to salt of NaCl, in general, this concept has not the expansion more.

It is possible to take advantage of those metrics in academic applications through the development of undergraduate students in their study, which can use those measurements outside the laboratory by learning how to calculate it and then applying them by comparing different metrics to the different procedures of the chemical reaction after trying many times to develop and improve it or from other different procedures (case study analysis), as well as to encourage researchers to adopt a friendly greener procedures for humans and the environment for the purpose of achieving sustainable development in the conservation of natural resources and thus preserve the rights and the safety and security of the environment in all aspects.

Generally, the application of green chemistry are directly related to three very important interrelated aspects of human life in a society, the economy and the environment, which directly contributes to the achievement of a better kind of life and to create a safe clean environment free of pollutions. [4]

From the point of view of industry, there is a great need to learn the chemists on the basis of green chemistry through workshops and seminars and thus the application of the twelve principles in all the earliest stages for the development of any industrial process.

The metrics of Gas-Chromatography (GC) technique is an important tool (tables and graphs) that clearly show changes and improvements taken over the development of an industrial stages, and also to analyze and follow up on those changes with time in the framework of green chemistry and sustainable development.

On the other hand, it can be used to compare and follow different paths of various industrial processes that have the same ultimate goal, and thus achieving the cost analysis and economic feasibility of any industrial project.[3-6]

Table 1. Example of Table in Academia

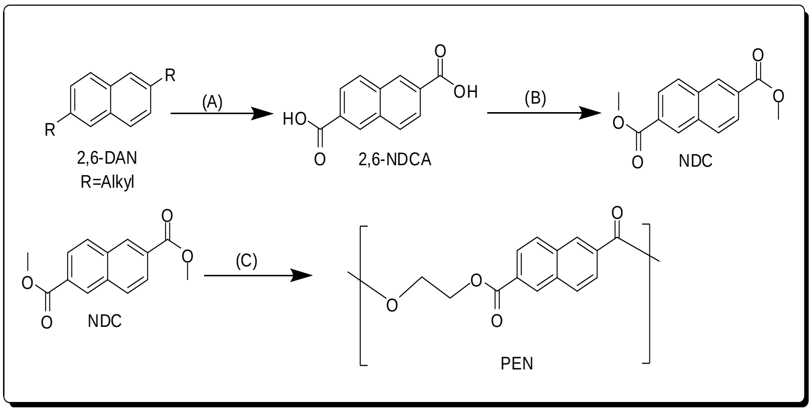
Metric	**Process no. 1**	**Process no. 2**
% Yield		
% Selectivity		
No. of steps		
No. of catalysts		
No. of solvents		
Organic vs. Aqueous Solvents		
Process Hazards		
Renewable Starting Materials		
E-Factor		
Atom Economy		
Atom Efficiency		
Effective Mass Yield		
Carbon Efficiency		
Reaction Mass Efficiency		

Table 2. Example of Table in Industry

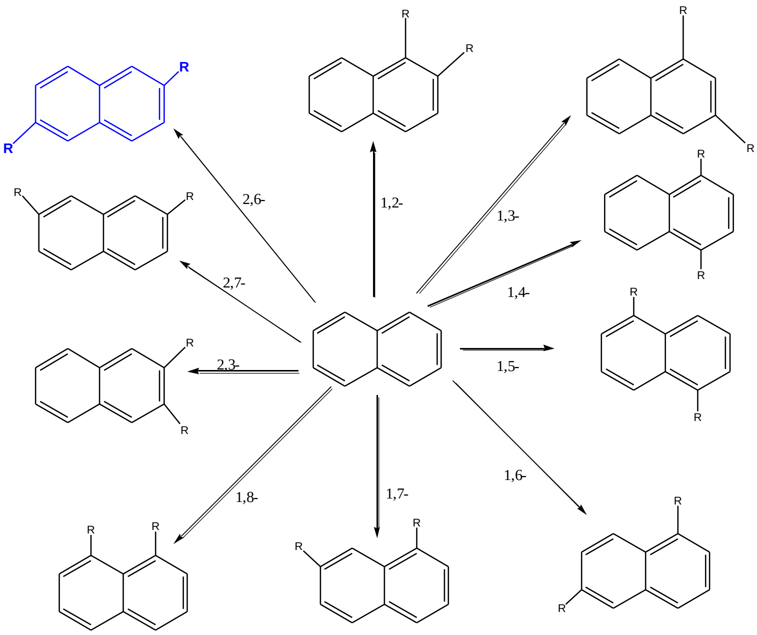
Metric	**Process no. 1**	**Process no. 2**
% Yield		
% Selectivity		
No. of steps		
No. of catalysts		
No. of solvents		
Organic vs. Aqueous Solvents		
E-F: Organic Waste per Kg product		
E-F: Aqueous Waste per Kg product		
Process Hazards		
Renewable Starting Materials		
Cost per Kg of product		
Atom Economy		
Atom Efficiency		
Effective Mass Yield		
Carbon Efficiency		
Reaction Mass Efficiency		

Results and Discussion:

Industry of polymers, One of the problems facing the chemical industry is the lack of production of PEN polymer (poly ethylene naphthalate) where the global production up to (20,000 tons per year), to the lack of efficient and clean method to prepare it, in addition to the difficulty of synthesis the precursor compound (2,6-dialkyl or methyl naphthalene) through alkylation reaction of naphthalene because of the formation possibility of ten dialkyl isomers at different positions of naphthalene molecule and thus the difficulty in separation and purification processes, waste produced, low yield, high cost, and pollution problems.[7,8]



Scheme 1. Production process for PEN from 2,6-DAN. (A) Oxidation. (B) Esterification. (C) Transesterification of NDC with ethylene glycol.



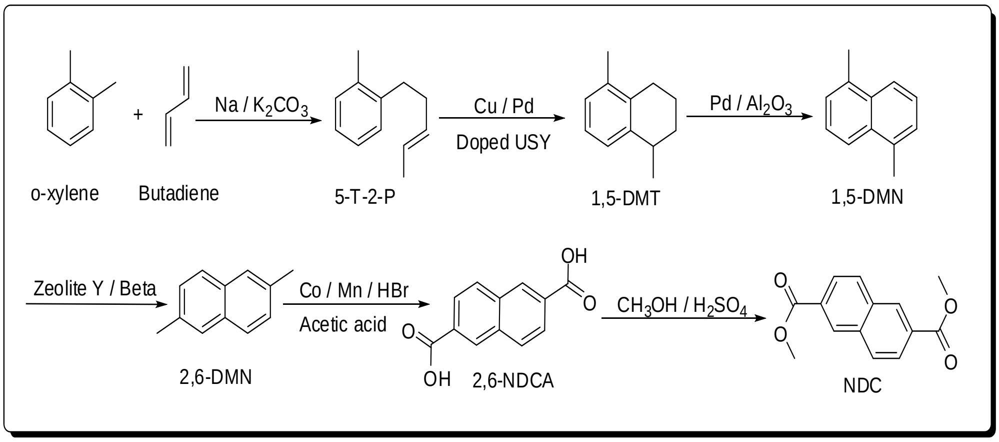
Scheme 2. The ten possible dialkyl isomer that could be formed during naphthalene dialkyllation.

From the literature review, there are many global companies using different industrial processes of 2,6-Dialkyl Naphthalene production (as a patents) with many advantages and disadvantages according to the following table.[9-14]

Table 3. Industrial method of synthesis 2,6-Dialkyl Naphthalene

Company	**Starting materials**	**Advantage**	**Disadvantage**
Amoco Chemicals	*o*-xylene and butadiene	Substrates are easily accessible and cheap.	Uneconomical in cost and yields.
Optatech [9,10]	*p*-xylene and butadiene	More economical route reducing the no. of steps.	Low yield (55%) and selectivity (24%).
Mitsubishi Gas Chemicals [11]	Acetylation of 2-methylnaphthalene	Low cost of substrates.	Large amounts of Lewis acid catalyst, poor yields.
NKK, Chiyoda	Direct alkylation of naphthalene by propylene	Naphthalene is available from crude oil fragments.	Possible formation of 10 different isomers, large amounts of Lewis acid, difficult handling and corrosion.

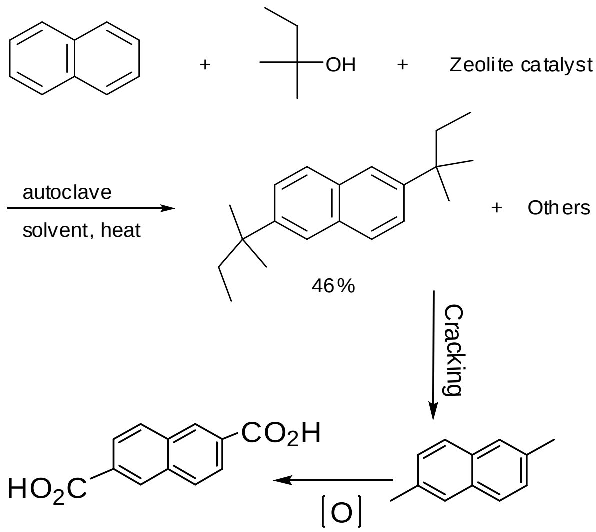
As example, US Amoco Chemical company[12,13] has developed one such process. It is a seven-step process (alkylation, cyclisation, dehydrogenation, isomerisation, separation, oxidation, esterification), which uses the readily available *o*-xylene as the starting material (Scheme 3).[14]



Scheme 3. The commercial production of Naphthalene 2,6-Dicarboxylate (NDC)

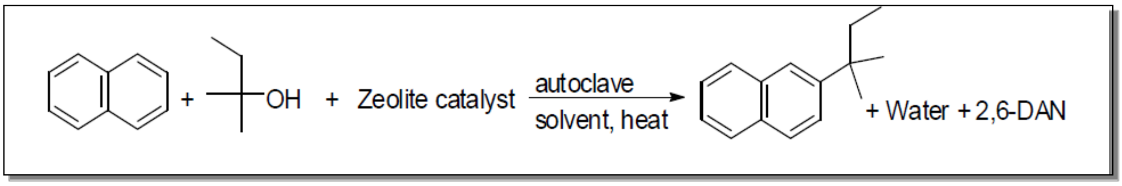
Recently, from published work by Keith Smith *et al.* (*Green Chem*. 2012),[6] in ever greener route of synthesis 2,6-dialkyl naphthalene through a selective reaction of direct alkylation of naphthalene using tertiary amyl alcohol over zeolite as a reused solid heterogeneous catalyst.

The global production of polymer material depends on the availability of 2,6-dialkylates naphthalene, especially substance 2,6-Dimethyl naphthalene (DMN). According to the literature,[15] the prepared tertiary-amyl compounds can be breaks up to give methyl derivatives directly, as in the following scheme.



Scheme 4. Direct selective alkylation of naphthalene over zeolite catalyst.

The above scheme is clear to show that at least four steps of alkylation processes from Amoco Chemicals' procedure are reduced by one step to give (70%) of 2,6-dialkyl naphthalene (2,6-DAN) mainly 2,6-di-*tert*-amyl naphthalene (46%) and useful side-products such as 2-*tert*-amyl naphthalene as a lubricant oil,[16] and water as a benign waste, according to the following equation.[8]

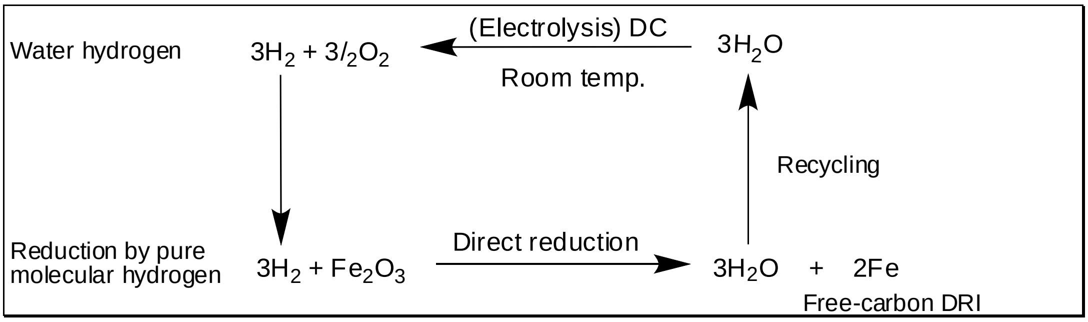


The above reaction and Scheme (4) are clearly showing the ever greenness manufacturing of useful products (2,6-dialkyl naphthalene and lubricant oil) along with water produced with no waste as a comparison with the commercial production of Amoco Chemicals company, as in Scheme (3).

Therefore, the present method offers great potential for improving the "greenness" and commercial viability of the production of PEN, although it would probably need to be converted into a continuous process.

Industry of Iron, global production of reduced iron about (73.3 million tons a year) spread over the following used techniques: (60.5%) US Midrex Company that based on the natural gas (H_2 ≈75% and CO ≈14%), (15.9%) Mexican HYL Company, and (23.6%) other methods which depend on coke (H_2≈50% and CO≈48%). Resulting from the use of natural gas and coal in the reduction process of iron oxide ore large quantities of carbon dioxide (CO_2) gas (3×10^5 and 6×10^6 ton / year).[17, 18]

While in contrast, from green industrial aspects of Jaleel's (Iraq) process in providing free carbon-iron industry, this process can be considered as a greener approach to the sustainability development in the Iron industry worldwide.



Scheme 5. Jaleel's (Iraq) Process in Providing Free Carbon-Iron Industry

Jaleel K. Ahmed *et al.* 2013,[19] has been shown ever greener source of free carbon-reducing gas that is water hydrogen as pure H_2 >99% obtained from electrolysis process of alkaline water which is also produced ~98.5% oxygen gas as well as heavy water residue. The water hydrogen (>99% H_2) used in the production of directed reduced Iron (DRI) instead of reduced gas that produced from natural gas and coke, where the percentage (H_2 ≈75%, and CO ≈14%) and (H_2 ≈50%, CO ≈48%) respectively.

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

In the case of water source for reducing gas, no polluted gas is discharged to the atmosphere, while in the case of two traditional sources (natural gas and coke); huge quantity of carbon dioxide is produced (3×10^5 and 6×10^6 ton respectively) as a greenhouse gas contributing to climatic change.[18, 19]

$$Fe_2O_3 + 3CO \rightleftharpoons 2Fe + 3CO_2$$

$$C + CO_2 \rightleftharpoons 2CO$$

Conclusion:

The principles and metrics of green chemistry can be considered as a useful and important tool in the analysis of the "greenness" of all the chemical processes that take place in the industry or in the laboratory or even planning for new chemical reactions in the design stage.

In addition, the methods and metrics of green chemistry must have taught in academia because the constant exposure to these factors and metrics and learning how to calculate and compare with each other, have a valuable impact in the industry and thus stimulates on maintain the sustainability of chemical safety and security of laboratories at the university or in the factories in sector of industry, including those related clean, safe, healthy, and green operations for humans and the environment in which they live.

الكيمياء الخضراء واستدامة الأمن والسلامة الكيميائية

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الخلاصة:

وفقا لمبادئ العلوم الحديثة الصديقة للبيئة الاثني عشر التي تسمى "الكيمياء الخضراء" جنبا إلى جنب مع المقاييس البيئية العملية والتي من الضروري أن تستخدم من أجل تطوير وتحقيق، وأداء استدامة السلامة الكيميائية والأمن، من خلال تطبيق هذه المقاييس العملية في كل من الأوساط الأكاديمية والصناعة.

الكلمات المفتاحية:

الكيمياء الخضراء، مبادئ العلوم الحديثة الصديقة للبيئة الاثني عشر.

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