EDUCATION IN GREEN CHEMISTRY : INCORPORATING GREEN CHEMISTRY IN SCHOOL CURRICULUM

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There is a sufficiency in the world for man's need but not for man's greed. Mahatma K. Gandhi

In the midst of a more vigorous concern for the environment, several terms have been put forward to capture an important idea. They represent the supposition that chemical processes that carry environmental negatives can be replaced with less polluting or non-polluting alternatives. Chemistry has historically been part of the problem, but now we hope it can be part of the solution. Here, the term "Green Chemistry" will be the focus since it is now the most widely used term. The Green Chemistry is a perfect fit for a school curriculum committed to the well-being of its responsible citizens with core human values. The principles of Green Chemistry that can energise our classrooms and bring long-term meaning and direction to a component of academic research await clear definition. This paper has been prepared to help to introduce the concepts of Green Chemistry in school curriculum and to give students and teachers a chance to think about the field of chemistry from a different perspective.

What is Green Chemistry?

Green Chemistry is a pro-active approach to pollution prevention. It targets pollution at the design stage, before it even begins. If chemists are taught to develop products and materials in a manner that does not use hazardous substances, then much waste, hazards and cost can be avoided. Green Chemistry is designing chemical products and processes that reduce or eliminate the use and/or the generation of hazardous substances. The term "Green Chemistry", as adopted by the IUPAC Working Party on Synthetic Pathways and Processes in Green Chemistry, is defined as: "The invention, design and application of chemical products and processes to reduce or to eliminate the use and generation of hazardous substances". Think about the simple equation of risk: Risk = Hazard x Exposure. Traditional approaches to pollution prevention focus on mitigating the hazard or end-of-pipe pollution

prevention controls. These traditional technologies focus on limiting the exposure of a hazardous material. Unfortunately, exposure precautions can and will fail (i.e., gloves can tear, goggles can break, chemical releases can occur). Green Chemistry goes to the root of the problem and aims to eliminate the hazard itself. Green Chemistry is the only science that focusses on the intrinsic hazard of a chemical or chemical process. It seeks to minimise or eliminate that hazard so that we do not have to worry about exposure.

Why Green Chemistry in School?

Green Chemistry is an ideal focus for school science education because it

- ^l presents a modern version of the traditional chemistry curriculum;
- uses less toxic materials, making experiments safer for students;
- teaches critical thinking skills;
- reduces cost with less expensive solvents and equipment and fewer toxic waste disposal fees;
- merges scientific concepts with sustainability and responsible human;
- gives school students opportunities to participate in meaningful science fair and projects.

What is the difference between Environmental Science and Green Chemistry?

Both areas of study seek to make the world a better place. The two are complimentary to each other. Environmental Science identifies sources, elucidates mechanisms and quantifies problems in the earth's environment. Green Chemistry seeks to solve these problems by creating alternative, safe technologies. Green Chemistry is not Environmental Chemistry. Green Chemistry targets pollution prevention at the source, during the design stage of a chemical product or process, and thus prevents pollution before it begins.

Is Green Chemistry more Expensive than Traditional Chemistry?

No. A simplified analysis of the cost structure associated with any chemical process takes into account the cost of materials, equipment and the human resources necessary. But, in reality, disposal, treatment, and regulatory costs associated with the buying, using, and generating hazardous materials involves numerous hidden costs. When you buy and use a hazardous material you are paying for it twice, once when you use it and once when you get rid of it. It makes sense that if you use materials that are non-hazardous and thus have minimal regulatory or disposal costs associated with them, the benefit to the economic bottom line is obvious. The Green Chemistry challenge has provided illustrations of several examples where industry has not only accomplished goals of pollution prevention, but has achieved significant economic benefits simultaneously.

How Chemists are Taught Green Chemistry?

One way that chemists are learning how to do Green Chemistry is by following the 12 principles of Green Chemistry. There are a set of guidelines that chemists use in order to perform chemistry

in a better way. As you take a closer look at them, you will find they are very intuitive and simply good to practice.

The 12 Principles of Green Chemistry

1. Prevention

This principle is the most obvious and over- arches the other principles. It goes back to the old adage, "an ounce of prevention is worth a pound of cure". It is better to prevent waste than to clean it up after-the-fact. Throughout the history there have been many cases of environmental disasters that demonstrated this (Bhopal, India; Love Canal; Times Beach; Cuyahoga River).

2. Atom Economy

This principle gets into the actual chemistry of how products are made. As chemists, atoms are assembled to make molecules. The molecules are assembled together to make materials. This principle states that it is best to use all the atoms in a process. And, those atoms that are not used end up as waste. The atom economy is a simple calculation that can be used when teaching stoichiometry and chemical reactions. The calculation is: A.E. = Formula Weight (FW) of product divided by the FW of all of the reactants. It is a simple measure of the amount of waste in a process.

3. Less Hazardous Chemical Synthesis

This principle is focussed on how we make molecules and materials. The goal is to reduce the hazard of the chemicals that are used to make a product (there agents). Throughout the history of how we have invented products and developed the

process for making them, chemists have traditionally not thought about what reagents they are using and the hazards that are associated with them. Chemists have traditionally used whatever means necessary. Today, we are finding that less hazardous reagents and chemicals can be used in a process to make products… and, many times they are made in a more efficient manner!

4. Designing Safer Chemicals

The previous principle was focussed on the process. This principle focusses on the product that is made. Everyone wants safe products. Everyone also wants products that do what they are supposed to do (they have to work!). This principle is aimed at designing products that are safe, non-toxic and efficacious. A good example of this is pesticides; which are products that are designed to be toxic. Many researchers are focussed on creating pesticides that are highly specific to the pest organism, but non-toxic to the surrounding wildlife and ecosystems.

5. Safer Solvents and Auxiliaries

Many chemical reactions are done in a solvent. And, traditionally organic solvents have been used that pose hazards and many are highly toxic. They also create volatile organic compounds (VOC's) which add to pollution and can be highly hazardous to humans. This principle focusses on creating products in such a way so that they use less hazardous solvents (such as water). We use solvents regularly in our daily lives (cleaning products, nail polish, cosmetics, etc.) and in the chemistry laboratory. An example that many can relate to, is that of nail polish products. Have you walked by a nail salon and caught a smell of the solvents that are used? The solvents traditionally

used have potential toxicity and are certainly not pleasant to smell. A water-based alternative polish would avoid the exposure that goes along with the nail polish and reduce the hazards associated with traditional products.

6. Design for Energy Efficiency

Today, there is a focus on renewable energy and energy conservation. We use energy for transportation purposes and to provide electricity in our homes and businesses. Traditional methods for generating energy have been found to contribute to global environmental problems such as global warming and the energy used can also be a significant cost. This principle focusses on creating products and materials in a highly efficient manner and reducing the energy associated with creating the products, therefore, reducing associated pollution and cost.

7. Use of Renewable Feedstocks

Most of the products we use in our everyday lives are made from petroleum. Our society not only depends on petroleum for transportation and energy, but also for making products. This principle seeks to shift our dependence on petroleum and to make products from renewable materials that can be gathered or harvested locally. Bio-diesel is one example of this where researchers are trying to find alternative fuels that can be used for transportation. Another example is alternative, bio-based plastics. Polylactic Acid is one plastic that is being made from renewable feedstocks such as corn and potato waste.

8. Reduce Derivatives

This principle is perhaps the most abstract principle for a non-chemist. The methods that chemists use to make products are sometimes highly sophisticated. And, many involve the manipulation of molecules in order to shape the molecules into what we want them to look like. This principle aims to simplify that process and to look at natural systems in order to design products in a simplified manner.

9. Catalysis

In a chemical process, catalysts are used in order to reduce energy requirements and to make reactions happen more efficiently (and many times quicker). Another benefit of using a catalyst is that generally small amounts (catalytic amount versus a stoichiometric amount) are required to have an effect. And, if the catalyst is truly a "green" catalyst it will have little to no toxicity and it will be able to be used over-and-over again in the process. Enzymes are wonderful examples of catalysts that have been proven to perform amasing chemistry – our bodies are wonderful examples! Green chemists are investigating using enzymes to perform chemistry in the laboratory in order to obtain the desired product. Many times enzymes will have reduced toxicity, increased specificity and efficiency.

10. Design for Degradation

Not only do we want materials and products to come from renewable resources, but we would also like them not to persist in the environment. There is no question that many products we use in our daily lives are far too persistent. Plastics do not degrade in our landfills and pharmaceutical drugs such as antibiotics build up in our water streams. This principle seeks to design products in such a way, so that they perform their intended function and then, when appropriate, will degrade into safe, innocuous by-products when they are disposed of.

11. Real-time Analysis for Pollution Prevention

Imagine if you have never baked a cake before in your life and you did not have a cookbook to refer to. You mix the ingredients that you believe you need and you place the cake in the oven. But, for how long do you cook it and at what temperature? How will you know when the cake is done? What happens if you cook it too long or for not enough time? This process is similar to what chemists have to do when they make products. How long do they allow the reaction to run for? When do they know that it will be 'done'? If there was a way to see inside the reaction and to know exactly when it would be done, then this would reduce waste in the process and ensure that your product is 'done' and is the right product that you intended to make.

12. Inherently Safer Chemistry for Accident Prevention

This principle focusses on safety for the worker and the surrounding community where an industry resides. It is better to use materials and chemicals that will not explode, light on fire, ignite in air, etc., when making a product. There are many examples where safe chemicals were not used and the result was a disaster. The most widely known and perhaps one of the most devastating disaster was that of Bhopal, India in 1984 where a chemical plant had an accidental release that resulted in thousands of lives lost and many more injuries. The chemical reaction that occurred was an exothermic reaction that went astray and toxic fumes were released to the surrounding community. When creating products, it is best to avoid highly reactive chemicals that have potential to result in

accidents. When explosions and fires happen in industry, the result is often devastating.

Teacher's Guide to Activities

The first activity can begin with asking simple questions (that do not have right or wrong answers) to get the students to think about what a chemist does and their role in solving global environmental problems. The questions can be asked at the beginning of class and they can write down their initial answers. The questions can be asked again at the end of the Green Chemistry module to see if their perspectives have changed. After introducing the 12 principles to the students, the second activity can help them to come to a better understanding of the principles. By working alone, or in groups, they can re-write the principles so that they are understandable to them and to their classmates. The activity sheet given below can give them the extended principles that are written so that a chemist can understand them. How will they re-write them so that anyone can understand?

Student Module: An Introduction to Green Chemistry

Activity 1: Questions to think about before we begin

- 1. What does a chemist do?
- 2. What are some chemical products?
- 3. What do you think about when you hear the words "Green Chemistry"?
- 4. What is environmental science?

- 5. Do you think our world has environmental problems? What are those problems?
- 6. How do you think we will go about solving those problems?

Activity 2: The Twelve Principles of Green **Chemistry**

Now that you have learned about what Green Chemistry is, think about what it means to you. Re-write the 12 principles in your own words so that they are understandable to you and your classmates.

1. Prevention

It is better to prevent waste than to treat or clean up waste after it is formed.

2. Atom Economy

Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Synthesis

 Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.

6. Design for Energy Efficiency

Energy requirements should be recognised for their environmental and economic impacts and should be minimised. Synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.

8. Reduce Derivatives

Unnecessary derivatisation (blocking group, protection/ deprotection, temporary modification of physical/ chemical processes) should be avoided whenever possible.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.

11. Real-time Analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substance and the form of a substance used in a chemical process should be chosen so as to

minimise the potential for chemical accidents, including releases, explosions and fires.

Green Chemistry experiments use and produce fewer toxic chemicals than traditional chemistry experiments, and they're also safer and less expensive to perform. It is now high time for us to think about (i) the areas of Green Chemistry that were often neglected, (ii) the value of integrating Green Chemistry principles in today's curricula, and (iii) strategies educators might use to incorporate Green Chemistry in their classrooms. We have outlined areas of scientific knowledge that we believe to be of vital importance for the education of future chemists and others. Green Chemistry has the potential to recruit innovative and energetic students, repair a damaged public image, and bolster the long-term prosperity of the chemical sector on the domestic and international scale. We argue that teaching traditional chemistry in a new way is the most effective way to achieve these ends. A new series of teaching principles and tools necessary to implement this change are discussed with emphasis on the long range impacts of a chemistry education that is inherently green. General applications of Green Chemistry, including sustainability, product design, and toxicology should be discussed, while tools such as life-cycle analysis, atom efficiency, structure-activity relationships, and eco-design be emphasised. The goal of the paper is to educate students and enable them to incorporate these concepts into their personal endeavours.

A common belief among us is that our education would have been significantly enhanced with the incorporation of Green Chemistry, beginning at the elementary level and continuing throughout graduate course work. It is unfortunate that Green Chemistry is not addressed to a greater extent in

the chemistry curriculum. As the general public, political leadership, and the scientific community continue to recognise the environmental consequences resulting from decades of industrial production, chemists and chemical engineers find themselves uniquely positioned to lead the way to a sustainable future.

The Scientific Context

The science of chemistry is central to address the problems facing the environment. Through the utilisation of various sub-disciplines of chemistry and molecular sciences, there is an increasing appreciation that the emerging area of Green Chemistry is needed in the design and attainment of sustainable development. A central driving force in this increasing awareness is that Green Chemistry accomplishes both economic and environmental goals, simultaneously through the use of sound, fundamental scientific principles.

The International Context

Through the vehicle of Green Chemistry, IUPAC is engaging the international community in issues of global importance to the environment and to industry, through education of young and established scientists, provision of technical tools, governmental engagement, communication to the public and scientific communities, and the pursuit of sustainable development. By virtue of its status as a leading and internationally representative scientific body, IUPAC is collaborating closely in furthering individual national efforts as well as those of multinational entities. In this context, educational opportunities to train chemists in the scientific principles and technical methodologies

of Green Chemistry are, of course, of primary importance. To establish and carry out the Green Chemistry educational programmes, there needs to be a partnership among government entities, industry and academic institutions. This partnership should focus on the importance of development and dissemination of new science and technology that form the basis of Green Chemistry and on the related education and training. These target audiences need curriculum materials to be developed and a suitable educational infrastructure in Green Chemistry to be made available to teachers, instructors and professors.

Need for Workshop on Green **Chemistry**

Existing government and industry programmes (R and D, awards, information, tools, etc.) useful for incorporating Green Chemistry into the education systems should be studied.

Task: We need to develop a survey and collect information among the participants on the existence of programmes and materials on Green Chemistry. Report on existing collaborations among international organisations (educational and industrial communities) for incorporating Green Chemistry concepts into the education system. Identify the existing Awards dedicated to Green Chemistry that stimulate education, information exchange and promotion of Green Chemistry to the public. The outcome will be an account that will illustrate the actions and programmes on Green Chemistry for incorporating these new concepts into the educational system.

Existing Green Chemistry educational material, tools, initiatives and sources should be studied. Tasks : Identify (and assess) the existing Green Chemistry educational sources (e.g., university programmes, scientific societies, government programmes, industrial programmes, schools, etc). Identify educational material and tools suitable for scientific faculties belonging to the Universities involved in Green Chemistry programmes.

Outcome: A resource guide of existing Green Chemistry educational materials and tools.

Commitments and recommendations are necessary to carry out Green Chemistry educational programmes should be studied.

Tasks: Recommend future initiatives and programmes on Green Chemistry Education, specifying mechanisms, tasks and tools to implement them.

Outcome: A list of possible recommendations in order to stimulate education communities as well as industrial and governmental interests in the mechanisms that are available or that need to be created to incorporate Green Chemistry effectively into the education systems.

Educational areas that address Green Chemistry Education should be studied.

Tasks: Identify educational areas that address Green Chemistry Education, in particular: Scientific (with a specification of the different levels), industrial (with a specification of the different kinds of training), general public (to improve the awareness of the benefits deriving from the Green Chemistry approach), business (to explain and demonstrate the benefits for the market deriving from the Green Chemistry approach), Government (to identify the appropriate channels to involve government in the adoption of national Green Chemistry educational programmes/projects/activities).

Outcome: An account will illustrate the mechanisms required to promote the incorporation of Green Chemistry concepts into various levels of chemical education.

Elaborating and carrying out the Green Chemistry educational programmes/projects with new educational materials/tools should be studied. Tasks : Identify the Green Chemistry educational programmes/projects, such as curriculum materials, teacher training, targeted funding, outreach mechanisms, etc. Identify new materials/ tools for Green Chemistry Education with more emphasis on new types of educational courses on Green Chemistry, such as new e-technologies (i.e., groupware applications, digital libraries, etc.).

Outcome: An account will illustrate the Green Chemistry educational programmes/projects and the benefits of new materials/tools for a faster and wider dissemination of Green Chemistry concepts.

A Guide for Green Chemistry Education should be prepared. As the principal workshop outcome, a background document explaining the barriers, needs, and benefits of Green Chemistry Education will be developed. It will illustrate the scientific and social potential of Green Chemistry. The resulting document will constitute a guide for Green Chemistry Education, a reference for the programmatic future educational initiatives in the context of Green Chemistry.

Green Experiments

- Solvent less Aldol reaction
- A greener bromination of Stilbene
- Synthesis and recrystallisation of adipic acid
- **.** Gas-phase and microwave synthesis and metallation of 5,10,15,20-etraphenylporphyrin
- ^l Thiamine-mediated benzoin condensation of furfural
- Patterning surfaces with molecular films
- \bullet \quad Liquid CO $_2$ extraction of natural products
- ^l A Diels-Alder reaction in water
- The use of supercritical carbon dioxide as a green solvent.
- Aqueous hydrogen peroxide for clean oxidations.
- The use of hydrogen in asymmetric synthesis.

Teacher's View on the Twelve Points

- 1. Create no waste;
- 2. Nothing should be left over;
- 3. No toxicity;
- 4. Green products as well as non-green products have to work;
- 5. Get rid of all non-essential additives;
- 6. Reduce energy usage;
- 7. Use renewable materials;
- 8. Get rid of as many steps as possible;
- 9. Make use of a reusable method to speed up a reaction;
- 10. Use materials that break down in the environment (biodegradable);

- 11. Check everything you do against the other principles;
- 12. Safety first.

Benefits of Green Chemistry in the Curriculum

Future chemists and chemical engineers must be equipped with the tools necessary to support and promote global sustainability. Incorporation of the 12 principles of Green Chemistry into class material is essential for providing a solid basis for "green" approaches that are valid in both theory and practice. The 12 principles can be coupled with specific strategies to enhance and further complement the current chemistry curriculum. They also serve as a reminder that the chemistry we practice has social as well as environmental impacts. An increasing number of institutions are including Green Chemistry concepts in their curriculum, and some even offer degrees in Green Chemistry. The programmes at these institutions should be adopted by others and viewed as inspiration, helping to overcome some of the persistent counter-arguments to Green Chemistry in the classroom. Such arguments include "this is not the way the real world works"; "traditional material is more important than Green Chemistry concepts"; "there is not enough time to cover the traditional concepts and include new ones"; and simple reluctance to change. The benefits resulting from incorporation of Green Chemistry concepts are significant and applicable to all levels of education. Green Chemistry concepts provide a connection between the material taught in class and the students' everyday environment, far beyond pollution, ozone depletion and global warming. Some examples include the feasibility

and limitations of recycling, sustainability aspects of consumer product design, energy efficiency, and the ecological impacts of bioaccumulation and endocrine disruption in aquatic wildlife. With the full inclusion of Green Chemistry concepts, students of all disciplines, not just the chemical sciences, will have the ability to relate chemical concepts to the "real world" and to their chosen career path.

Implementation of Green Chemistry in the Curriculum

An important consideration often mentioned when curriculum modifications are proposed is the already overwhelming amount of information incorporated in chemistry education. We believe that Green Chemistry is not meant to replace existing class material or be taught as a separate section altogether. Instead, existing classes should be taught in a new way, incorporating key concepts into the curriculum to make chemistry inherently green. In a series of discussions, we identified a number of concepts that should be used to enhance the chemistry curriculum. Green Chemistry is not intended to be a solo discipline, but rather a means for conducting science in a responsible manner. It is not possible to track the fate of every chemical compound used and generated in a reaction or process. Environmentally benign chemicals are therefore highly desirable. Reactions should not only be evaluated based on conversion and selectivity, but also efficiency, sustainability, recyclability, degradation, and elimination or reduction of hazard. The connection between chemical structure and compound activity should be made

clear to students. Chemical functionality (sterics, electronics, hydrophobicity/philicity, toxicity) can provide a basic understanding of how chemicals impact the environment. An enhanced understanding of eco-toxicity and fates and transport of chemicals released to the environment is essential for the overall evaluation of chemical substances.

A curriculum that complements current teachings with the Green Chemistry principles is a first step in promoting the ideal that Green Chemistry is inherent to chemistry. These concepts will enhance the chemistry curriculum, providing understanding of the broader impacts of the chemical sciences, bridging gaps between the classroom and the global environment, and, most importantly, helping to complete the education of future chemists and engineers. Beyond the classroom and the individual, Green Chemistry requires an interdisciplinary awareness. A multidisciplinary approach to Green Chemistry education allows students to develop interdisciplinary communication and contacts early on, thus promoting concerted efforts for attacking problems and developing sustainable technologies with global awareness. The internet is an excellent resource that provides an incredible amount of information for global chemical and environmental news. Educators can utilise this tool to create an interactive classroom that allows students to learn in real time, to develop collaborations with students around the globe, and to teach themselves and others through peer-to-peer networks. We encourage educators to step outside their 'comfort zone' and embark on a mission of teaching these fundamental principles to their students. In doing so, many will find that they too will become students of Green Chemistry, just as we have.

Resources are already available to aid in the incorporation of Green Chemistry concepts into the curriculum, including texts, lab experiments, discussion topics, online resources, etc.

The Impacts

Today's students, and ultimately the scientific community of tomorrow, would significantly benefit from the introduction of Green Chemistry principles into the curriculum. Increasing communication and awareness among chemists, engineers, policy makers, and the general public will lead to a greater responsibility for environmental and global issues. Students will enter the professional world with knowledge of the weaknesses of current industrial processes, coupled with motivation for the development of solutions based on Green Chemistry principles in an international and interdisciplinary environment. Green Chemistry education can provide the required knowledge and awareness to develop the technologies that are necessary to achieve the ultimate goal of a sustainable world. It must be stressed that Green Chemistry should not be considered a discipline in itself but rather an approach for conducting science in a responsible manner so that future generations are not compromised by today's actions. Green Chemistry offers a systematic means to sustainable science based on chemical, environmental, and social responsibility while allowing creativity and innovative research to thrive. Interdisciplinary approaches, outreach programmes, recruitment initiatives, and the creation of a global community of educators are ways in which social perceptions of chemistry can be positively influenced. What we ask is that chemical education be enhanced by incorporating the ideals of Green Chemistry into

the curriculum, thus building a foundation that leads to a sustainable chemical enterprise and a sustainable society. With this new way of thinking about chemical education and research, students will be armed with the knowledge needed to effectively address the grand challenges of this twenty-first century.

Model Lesson Plan

Topic: Essentail Oil Extraction Using Supercritical CO₂

Many fruits and vegetables contain essential oils, which are water repellent or hydrophobic liquids that give the fruit or vegetable its distinctive fragrance. These essential oils are often extracted for use in perfume, cosmetics, food, medicine and house cleaning products. Many of these essential oils are extracted through liquid chemical extraction using dangerous chemical solvents, such as methylene chloride. Conventional methods used to extract essential oils include steam distillation or liquid chemical extraction. Steam distillation requires high energy input as energy is required to boil water to produce steam. The energy used combined with the dangers of heating large amounts of matter on an industrial level means that this process does not adhere to the principles of Green Chemistry. This is an important component of teaching students about Green Chemistry as it is not just a concept used in the lab but a concept meant to be used on an industrial scale to make products which are useful to the world. Steam distillation may seem like a benign process until it is evaluated against the 12 principles on an industrial scale.

Scientists have discovered the use of supercritical carbon dioxide (CO $_{\textrm{\tiny{2}}}$) at high pressure is an alternative method of extracting essential oils and that is the process which you will discover with your students through this activity. CO₂ is the gas exhaled by humans during respiration, is consumed by plants during photosynthesis and exists in the environment in abundance from human activity such as fossil fuel combustion.

It is important to note that the use of supercritical CO $_{\rm 2}$ for extraction does not affect the net amount of CO $_2$ in the environment, thus using supercritical CO $_{\textrm{\tiny{2}}}$ for essential oil extraction is not considered to affect climate change in anyway. Instead, the use of supercritical CO $_{\rm 2}$ is considered a greener way of essential oil extraction, since it reduces the amount of energy input and eliminates the need for dangerous solvents. Because supercritical CO $_{\textrm{2}}$ does not have high reactivity with essential oils, which can lead to the breakdown of the essential oil, its use in essential oil extraction is gaining popularity. Currently, supercritical CO $_2$ is used to remove caffeine from coffee beans to produce decaffeinated coffee and as a replacement for perchloroethylene in dry cleaning applications.

In this experiment, students will extract the essential oil d-limonene from the rind (skin) of lemon peels using both a steam distillation or simple distillation method and the method of using supercritical CO $_{\textrm{\tiny{2}}}$. They will analyse the difference between the two methods and make connections between the laboratory activities they do in the classroom and the industrial chemical processes that are used to make products. D-limonene gives lemons, oranges and limes their citrus-like scent.

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Educational Goal: To understand chemical, steam and CO $_{\rm 2}$ extraction methods and their relationship to green and industrial chemistry practices.

Student Objectives: Students will …

- extract essential oils from lemons using steam distillation;
- extract essential oils from lemons using supercritical CO₂;
- compute the use of energy in both extractions;
- compare the use of energy in both extractions;
- compare the use of hazardous chemicals in both extractions;
- \bullet Learn about phase changes of CO₂;
- Learn about extraction methods based on polarity.

Activities and Experiments: Cleaning up with atom economy

Cleaning up the environment and, more importantly, preventing pollution are important issues in today's world. Chemistry keeps us clean. One of the most fundamental of these solutions is

Extract essential oils from a lemon using steam distillation, supercritical CO₂ and organic solvent like CH $_{\rm 2}$ Cl $_{\rm 2}$

the application of the Green Chemistry principle of atom economy to chemical reactions. Atom economy moves the practice of minimising waste to the molecular level. Traditionally, chemists have focussed on maximising yield, minimising the number of steps or synthesising a completely unique chemical. Green Chemistry and atom economy introduce a new goal into reaction chemistry: designing reactions so that the atoms present in the starting materials end up in the product rather than in the waste stream. This concept provides a framework for evaluating different chemistries, and an ideal to strive for in new reaction chemistry. Atom economy means maximising the incorporation of material from the starting materials or reagents into the final product. It is essentially pollution prevention

at the molecular level, e.g. a chemist practising atom economy would choose to synthesise a needed product by putting together basic building blocks, rather than by breaking down a much larger starting material and discarding most of it as waste. Atom economy is an important development beyond the traditionally taught concept of per cent yield. Atom economy answers the basic question, How much of what you put into your pot ends up in your product ?

Associated Chemistry Topics

- Law of conservation of matter:
- Chemical reactions:
- Stoichiometry;
- Per cent yield;

Vocabulary

Atom Economy

1. The mass of desired product divided by the total mass of all reagents, times 100;

Per cent Atom Economy = (Mass of Desired Product / Total Mass of all Reagents) x 100;

- 2. The mass of desired product divided by the total mass of all products and byproducts produced, times 100; and
- 3. A measure of the efficiency of a reaction.

Per cent Yield : Actual yield divided by theoretical yield times 100

Theoretical Yield : The maximum amount of product that can be produced from the quantities of reactants used; the amount of a given product formed when the limiting reactant is completely consumed.

Stoichiometry – Application of the laws of definite proportions and conservation of mass to chemical processes; quantitative relationship between compounds involved in a reaction.

Saponification, or soap making, is a very old tradition, dating back to 2800 B.C. However, the chemistry was not described until the nineteenth century by the French chemist, Chevereul. Early

soap makers used animal fat and wood ash (which contains sodium hydroxide and potassium carbonate). Now a wide variety of materials and methods are available to the soap maker. Today, soap making is not only highly visible in the mainstream manufacturing industry (names like Lifebouy, Dove, Hamam), but many special product industries centre around handmade soaps as well. An excellent resource including the history, chemistry and manufacture of soaps and detergents is available from the Soaps and Detergents Association Web Site: http:// www.sdahq.org/cleaning/. Related information including stories about soap and detergent companies can be found at: http:// inventors.about.com/library/inventors/ blsoap.htm. A brief discussion, with excellent graphical models, of the chemistry of soap making can be found at: http:// antoine.frostburg.edu/chem/senese/101/ consumer/faq/making-soap.shtml. Clear directions, including pictures, for making soap are available at the Web Site: http:// www.soapcrafters.com/makebase.htm.

Now ask the students to calculate the atom economy for the saponification reaction by dividing the total mass of atoms utilised in the product by the total mass of all the reagents and

Saponification Reaction:

 $\text{CH}_3(\text{CH}_2)_{16}\overset{\text{O}}{\text{COCH}_2}$ O $\mathrm{CH}_3(\mathrm{CH}_2)_{16}\mathrm{COCH}_2$ O

Triglyceride of Stearic Acid

Sodium Hydroxide

Sodium Stearate (SOAP)

3 Na * [H3(CH $_2$) $_{16}$ CO] $3NaOH \xrightarrow{\text{Teau}/\text{Sult}} +$ O O

 $CH_3(CH_2)_{16}$ ĈOC H_2 and $HOCH_2CHCH_2OH$ OH

Glycerine (Glycerol)

Heat/Stir

multiplying by 100. Since, all the products produced are known, you could instead divide by the total mass of products and byproducts.

Questions

- 1. What is the atom economy for the saponification reaction, assuming 100 per cent yield (3 soap molecules for every triglyceride used)?
- 2. What is the atom economy if only two soap molecules were made (66 per cent yield) for every triglyceride molecule reacted (include

the third soap molecule in the waste instead of the product).

- 3. What is the theoretical yield (in grams) of soap, if 500.0 grams of the triglyceride of stearic acid are used?
- 4. What are some basic characteristics of reactions that have high atom economy?
- 5. Do you think it is more important to have high per cent yield or high atom economy? Why?
- 6. Describe modifications you would make to the saponification reaction to increase the atom economy.

Student Worksheet Name

Answers to Questions Calculated Atom Economy

1. 90.89%, see the following table:

Stoichiometric Coefficient. Name of Starting Material	Atomic Symbol, Quantity. Atomic Mass of Fach Atom	Mass (Quantity Times Atomic Mass) of All Atoms	Atoms Utilised in Product	Mass of Atoms Utilised in Product	Atoms Wasted in Byproducts	Mass of Atoms Wasted in Byproducts
1 Triglyceride of Stearic Acid	57C, 12.01; 110H, 1.008; 60, 16.00	891.45	36,70H. 20	534.92	21C, 40H, 40	356.53
13 Sodium Hydroride	3H, 1.008; 30, 16.00; 3Na, 22.99	119.99	2Na, 20	77.98		42.01
Totals:	57C, 113H, 3Na. 90	1011.44	36C, 70H, 2Na, 40	612.90		398.54
Product: 2 Sodium Stearate	36C, 70H. 2Na, 40	612.90			Atom Economy:	60.60%

2. 60.60%, see the following table:

- 3. 500.0 g SM / 891.45 g/mol SM = 0.5602 mol SM , 0.5602 mol SM 3 mol soap/1 mol SM = 1.681 mol soap, 1.681 mol soap 919.35 g soap/3 mol soap = 515.1 g soap
- 4. High atom economy characteristically involves rearrangement or addition (e.g. Diels-Alder, Claisen) rather than substitution or elimination processes (e.g. Wittig, Grignard), and makes use of catalytic rather than stoichoimetric reagents. Atom economical reactions incorporate as much of the starting materials as possible into the product, so solvent-free systems are another characteristic feature.
- 5. Open-ended question— Possibilities include: High atom economy might be preferred over high yield because it is more efficient and less waste is produced. High per cent yield might be preferred over high atom economy because more of the product is produced.

High yield with low atom economy might be preferred if a recyclable byproduct is formed.

6. Suggested answers, any logical reasoning is acceptable. Using a lower molecular weight base and/or a higher molecular weight triglyceride would reduce the mass of waste and/or increase the mass of the product, thus increasing the atom economy. Considering glycerol (glycerine) a product, rather than a byproduct would remove it from the waste accounting. Making soap directly from the fatty acid rather than the triglyceride would reduce the waste for this reaction, but where does the fatty acid come from?.

In an organic class, the atom economy could be calculated for all of the basic reaction types. Selectivity, per cent conversion, productivity, rates, catalysis and electrochemistry are all chemistry topics that would enhance this discussion of atom economy.

We have integrated several Green Chemistry experiments into the curriculum. The experiments themselves were just safer for the kids, and they got more out of it. They related to the concepts a lot easier than some of the other experiments we've tried in class, e.g. instead of creating or observing an obscure chemical reaction, students doing a Green Chemistry experiment in our class turned vegetable oil into bio-diesel fuel. Bio-diesel fuel is a concept that students understand. That really helps them connect what they're doing in the classroom with real life application, so they understand chemistry concepts faster and can remember them better. Providing high school teachers with experiments and resources is one of many ways we are spreading the word about Green Chemistry. And, curriculum development projects enhance the school's growing reputation as a leader in sustainable sciences.

Chemistry has been recognised as a scientific discipline for about 150 years, so the concept of Green Chemistry is relatively young by comparison. Because, the field is so new, there's an abundance of projects to work on. Many of those projects have focussed on curriculum development. Green Chemistry may be a relatively young discipline, but it has already gained a foothold in industry, where it is seen as a safer, less expensive, and more environmentally responsible way to conduct research and manufacture products. It's clear that consumers are expecting greener or more sustainable kinds of practices in producing the products they purchase. More importantly, applying the concepts of Green Chemistry can lead to safer, more efficient processes, which is exactly what every industry needs and wants. It's really cuttingedge stuff. It's really a need to know that we're doing something different and something new. The challenge, however, lies in the fact that there are very few Green Chemistry experiments, textbooks, and other teaching materials available at school level.

Further Readings

- ANASTAS, P. T. and J.C. WARNER. 2009. Green Chemistry: Theory and Practice, Oxford University Press, New York.
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- SCHWARZ, P., M. HUGERAT and M. LIVNEH. 2006. Chemistry Experimentation for All Ages. Arab Academic College for Education in Israel, Haifa, Israel.

Green Chemistry at http://greenchem.uoregon.edu/

- Real-World Cases in Green Chemistry, Volume II 37336-2, 2010 American Chemical Society, http:// webapplications.acs.org/portaltools/shopper/productDetail
- Atom Economy: A Challenge for Organic Synthesis, B.M. Trost, Angew.Chem. Int. Ed. Engl. 1995, 34, 259.

Online Resources

Chemistry Education Resources Science for Kids National Chemistry Week Chemists Celebrate Earth Day Chem Matters Magazine Green Chemistry Resource Exchange Greener Education Materials for Chemists (GEMs) University of Scranton's Teaching Green Chemistry Modules Green Chemistry Network

Featured Books

Handbook of Green Chemistry, ISBN/ISSN: 3527315772 Green Chemistry and Catalysis, ISBN/ISSN: 352730715X Green Chemistry: An Introductory Text, ISBN/ISSN: 0854046208 Green Chemistry: Theory and Practice, ISBN/ISSN: 0198506988 Advancing Sustainability through Green Chemistry and Engineering, ISBN/ISSN: 0841237786 Green Organic Chemistry, Strategies, Tools, and Laboratory Experiments, ISBN/ISSN: 0534388515