ACS Green Student Chapter Activity: Chemistry Demonstrations

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Sustainable and green chemistry in 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 substances.

It's important to note that the scope of these green chemistry and engineering principles go beyond concerns over hazards from chemical toxicity and include energy conservation and waste reduction, as well as life cycle considerations such as the use of more sustainable or renewable feedstocks and designing for end of life or the final disposition of the product.

By incorporating sustainable and green chemistry into your student chapter's activities you can:

- Become a spokesperson on your campus for sustainability and the solutions chemistry can bring through green chemistry
- Start a movement of sustainability across your campus and in the community
- Make a difference through chemistry
- Have a positive impact on human health, the environment & the future
- Improve the "image" of chemistry

Chapters who engage in at least three green chemistry outreach and educational activities during the school year are eligible to win a Green Chemistry Student Chapter Award.

Green Chemistry Themes to Consider[1]

Prevent waste than to treat or clean up waste after it is formed
Minimize the amount of materials used in the production of a product
Use and generate substances that are not toxic
Use less energy
Use renewable materials when it makes technical and economic sense
Design materials that degrade to innocuous products at the end of their usable life

Safety Note: Never work in the lab alone! Always have a faculty member, such as your student chapter sponsor/advisor, oversee your project plans. Follow all safety protocols required by your college or university when conducting these experiments and demonstrations.

[1] Middlecamp, Catherine, ed. *Chemistry in Context: Applying Chemistry to Society*. 8th ed. New York: McGraw Hill, 2014. Print

Demonstrations, like advanced versions of show-and-tell, are a classic method of communication: the familiar format of a demo and the excitement generated by chemistry displays is a great way to instill curiosity in a general audience. Once the audience's attention has been grabbed it's simple to transition into a broader discussion about green chemistry that is more likely to be remembered (and probably better attended) than a stand-alone lecture. Whether the demonstration is to be part of a symposium, workshop, or other type of event this document will provide everything needed to carry it out successfully.

General Tips for the Presenters

There are a few things to keep in mind when presenting on any subject.

1. Practice what you want to say ahead of time for better organization. If technology is involved, make plans for outlets, projectors, etc. ahead of time. Never perform a demonstration you haven't successfully tried beforehand.
2. Briefly introduce yourself – year in school, degree pursued, primary areas of interest, etc.
3. Ask the audience some questions to understand their level of knowledge and to engage them. Invite them to ask questions at any point during the talk.
4. Give the title and an overview of the demonstration; address briefly what the overall process will be and why it is important to attendees.
5. Describe each step and then show it so the audience can follow what is happening
    - i. Explain the purpose of the step
    - ii. How it is going to happen
        1. Your actions
        2. The chemistry taking place
6. Keep eye contact with the audience and try not to depend on index cards or notes.
7. Speak loudly, clearly, and not too quickly.
8. Repetition is key – identify the focus points of the demonstration and refer to them throughout.
9. Summarize.
10. Allow time for questions and discussion.
11. Thank the attendees for coming.

If possible:

- Allow volunteers from the audience to participate. (Can you provide lab coats or goggles?) Consider whether or not the resources are available to make the demonstration into a hands-on experiment for whole-audience participation, either individually or in small groups of 3-4.
- Include a visual such as a poster, model or diagram. If visuals are used be sure they are both explained and clearly visible to the audience.
- Provide follow-up materials such as handouts of the 12 Principles of Green Chemistry which are available for printing on the GCI website or the Easy Lab Fixes available on the University of Toronto Green Chemistry Initiative website
- At some point, have members of the audience break into groups to discuss a concept, brainstorm ideas, or play a game. Invite a few to share what they've talked about.
- Divide responsibility among members of your student chapter. One member may be able to make posters, another to find a venue, etc.
- If small objects are involved in the demonstration, try to obtain a camera that can project what you're showing onto a larger screen. Many lecture halls will be equipped with these cameras.

Advertise

Who will attend your demonstration if no one knows about it? One of the most important parts of hosting an event is advertising. Here are a few tips for getting better attendance when designing posters or spreading the word online.

1. Remember, you will know the material you're presenting better than anyone looking at your flyers, posters, or probably even in attendance. Sometimes it's best to take a step back when you're very familiar with the material. Think of how undergraduates, professors, high school teachers, etc. who have never heard of green chemistry would perceive it and tailor your message around the perceptions of the intended audience. Do some research to find out what they are most likely to care about and adjust the program to fit their needs. If you're presenting to professors, for example, they might be concerned about how this new material will fit into their already busy curricula.
2. Always approach advertising in a way that is SIMPLE, DIRECT, and RELEVANT. You don't need a sassy/witty marketing push. Stick true to your message and the purpose of the demonstration. People can instantly sense authenticity so try and be as clear as possible.
3. Make sure you have information access points for your program, such as a Facebook page, Tumblr or WordPress sites to give a more behind-the-scenes look. Also try to get your own URL and make it as short as possible for advertisements.
4. If you have an online presence, make sure all the facts are straightforward and easy to find. A simple page with the main details (time, date, place, description) and contact information should suffice. Find a tech-savvy friend to help you set up a website if you aren't sure how. There are a number of fairly simple drag and drop webpage builders.

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Additional Points to Consider When Developing a Demonstration for the ACS Green Student Chapter Award:

- **What are the main ideas you want to communicate? What visuals are appropriate and add to, rather than distract from, this communication?** Don't try to cover *everything*. One demonstration can be relevant to a variety of topics but it's more straightforward to pick two or three that you think are the most important for informing the audience about green chemistry.
- **Who is the audience? What level of chemistry knowledge is anticipated?** If it's a group knowledgeable about green chemistry, such as at a green chemistry workshop, less time should be spent introducing the subject. If presenting to an interdisciplinary audience, more time should be spent covering the basics such as the principles of green chemistry and benign chemical and process design. In any case, providing "real-life" examples will peak interest among the group.
- **How long will it be?** A total time 20-30 minutes (demo + discussion) is typically a good length.
- **Where should the demonstration be done**? In a lecture hall, outdoors, a classroom, etc.? Consider the amount of space needed for set-up and how many attendees you expect. If you plan on having a hands-on demonstration be sure there are tables or counters available. Also plan on reserving the location in advance.
- **How can you leave the audience feeling empowered and generate a feeling that they gained something by attending?** That might be a literal something such as a bottle of d-limonene scented hand sanitizer they can take home or a message they want to communicate to friends, co-workers, etc. Encourage the audience to use social media to share what they found interesting or motivating.
- **Consider how you might respond to someone who asked "so what?"** Make sure you've done research and provided examples of how the green chemistry in your demonstration is applicable to anyone.
- **Green Chemistry is not the same as Sustainability** – while there are overlaps between green chemistry and sustainability/environmental friendliness, keep in mind that as a candidate for the ACS Green Student Chapter award the focus on your activity should be specifically green *chemistry*.

Practical Check–list

Have you:

- ☐ Reserved a venue
- ☐ Acquired all necessary materials
- ☐ Researched the subject
- ☐ Practiced the demonstration
- ☐ Advertised
- ☐ Created visuals (if using)

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Constructing a Blackberry Solar Cell

(adapted from Beyond Benign)

A discussion about the effects of manufacturing emissions can be easily integrated into a demonstration where a solar cell is built and tested. If materials are available, each member of the audience or class can construct their own solar cell and test how well it was put together. Alternative energy, redox chemistry, crystal structures, biotechnology, production impacts, benign design, and photosynthesis are all relevant topics in the context of solar cells. Again, pick two or three topics to focus your talk.

Materials

1 transparent indium tin oxide conductive glass slide (ITO slide), 15mm x 35mm x 1mm
1TiO_2 coated indium tin oxide conductive glass slide, 15mm x 35mm x 1mm
1/2 drop of iodide electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine in propylene glycol)
2 small binder clips
1 blackberry (frozen, thawed blackberries work well)
1 small spatula
1 graphite pencil
1 piece of parafilm, cut into 20mm x 40mm in size
1 small aluminum dish pan (2 inches)
1 paper towel
1 razor blade
Multimeter
Light source (flashlight or sunlight)

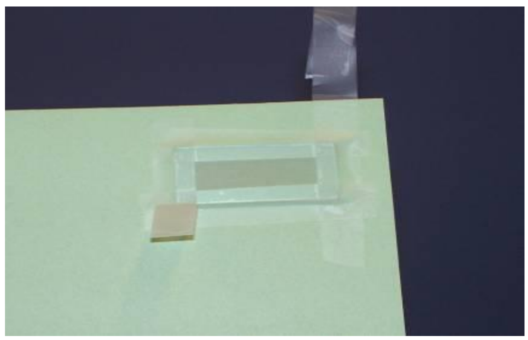
Note: Handle the glass plates by the edges to avoid touching the faces of the plates.

Preparation in the weeks leading up to the demo:

- Select and/or reserve the area/room in which you plan on holding the demonstration.
- Order or acquire indium tin oxide conductive glass slides. Ask if there are any available for you to use or discuss options for placing an order.
- Read up on the subject to prepare yourself for any questions from the audience and to build confidence for your presentation. Suggested articles include:
  - Solar Panels Pose and Environmental Hazard, Claims Report (2009): http://venturebeat.com/2009/01/14/solar-panels-pose-an-environmental-hazard-claims-report/
  - Solar panel production often requires harmful chemicals but advances in process chemistry are helping offset impact (2013): http://www.dw.de/despite-bright-potential-solar-power-struggles-to-stay-clean/a-16858170
  - Innovation for infrastructure with solar roadways (2014): http://abcnews.go.com/Technology/wireStory/inventor-pushes-solar-panels-roads-highways-24516959
  - Advertise.

Preparation the day of:

- Purchase frozen blackberries from any grocery store.
- Prepare iodide electrolyte solution (0.5 M potassium iodide mixed with 0.05 M iodine in propylene glycol). Propylene glycol is more environmentally friendly than its counterpart, ethylene glycol. Both are used in antifreeze.
- Determine which sides of the slides are coated with ITO using a multimeter with its setting placed on resistance (Ω). The side that creates a current is the coated side. Leave this face up on a paper towel.
- To make the TiO_2 coated slide:
  - Cover the glass with tape and secure the glass to the table. To do this, you will "mask", or cover, the glass with 2mm of tape on 4 sides. Secure the glass by adhering the free side of the tape to the table at a 45° angle. Your glass should look like the diagram below.

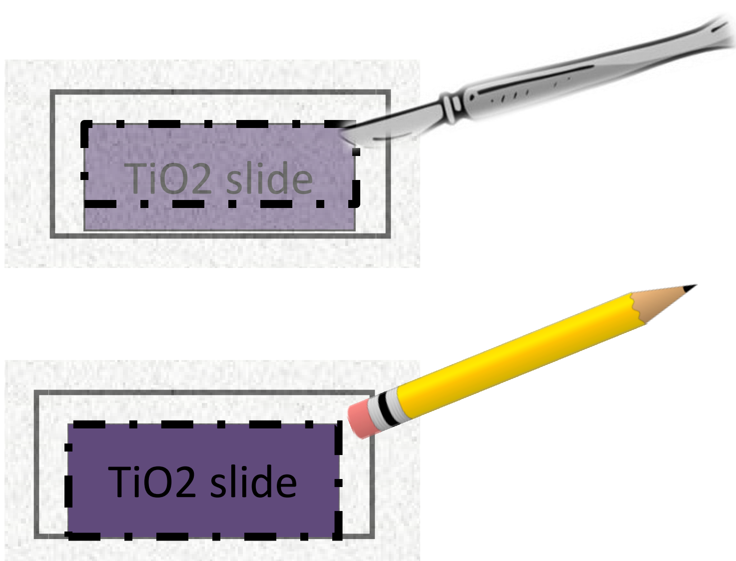


  - Wearing gloves, prepare TiO_2 paste and coat the inside 80% of the conductive plate leaving a 2 mm border all the way around the slide. Paste is produced by mixing:
    - 15% TiO_2, 0.7 % trimesic acid (1,3,5-tricarboxylbenzoic acid)
    - 84.3 % water by mass
    - Add the TiO_2 and trimesic acid and water to a ceramic jar.
    - Add approximately 15 ceramic beads
    - Place on ball mill and allow mixture to run for approximately 12 hours
    - Add 1-2 drops of the TiO_2 solution uniformly to the conductive glass and spread it across the glass using the body of a stirring rod until the glass is covered completely.
    - Allow the TiO_2 to dry for 10 minutes before removing tape slowly as to not damage the conductive glass.

Demonstration Procedure

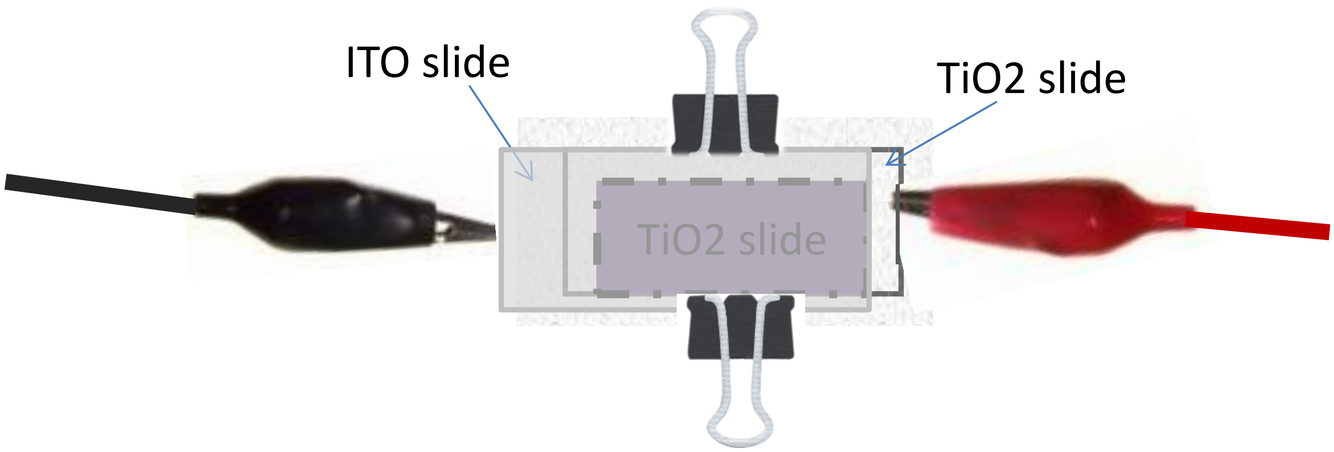
(adapted from Beyond Benign)

1. Place the blackberry in the aluminum pan. If using a camera to project the demonstration ensure at this time that it is in the correct position.
2. Using a spatula, crush the blackberry to extract the juices. Scoop out the solid pulp.
3. Remove the glass slide containing the white TiO_2 coating from its bag. **Handle the glass slide by the edges only**. Determine which side the TiO_2 coating is on.
4. Place the glass slide with the TiO_2 face down into the aluminum pan. Allow to sit for 3-5 minutes making sure the TiO_2 coating is completely covered in juice.
5. Take advantage of the 3-5 minutes of waiting time to ask the audience questions or explain the process in more detail. See if they have any questions so far.
6. Remove the ITO coated glass slide from its bag. Determine which side the coating is on by using a multimeter with its setting placed on resistance (Ω). The indium tin oxide coating is on the side of the slide that gives a non-zero reading on the multimeter.
7. Using the tip of a graphite pencil, lay down the carbon catalyst by shading the indium tin oxide coated side of the slide paying additional attention to the short edges of the slide. It's okay if the graphite is not visible; the carbon atoms have been applied.
8. Remove the TiO_2 slide from the blackberry juice. Use the paper towel to gently blot the excess juices off the slide. Dry the slide as much as possible, but do not remove any of the TiO_2 coating (i.e. dab not wipe).
9. Remove and discard the wax paper backing from the parafilm and place the parafilm on top of the dye coated TiO_2 slide. Use the eraser end of the pencil to press the parafilm to the glass slide in the area that borders the TiO_2
10. Using a razor blade carefully cut out the area of the parafilm that sits on top of the TiO_2. Press lightly with the blade, so that the conductive coating does not scratch off. Reinforce the parafilm seal around the edges of the TiO_2 area with the eraser end of the pencil.



11. Place 1/2 drop of the iodide electrolyte solution on top of the TiO_2. The parafilm should act as a well that prevents the electrolyte solution from leaking out.
12. Place the ITO coated glass slide on top of the TiO_2 slide so that the conductive sides face each other. Stagger the slides so that as much of the glass slide as possible is exposed and the entire TiO_2 is covered.

13. Use the 2 small binder clips to hold the slides together. Attach the clips on the longer sides.
14. Carefully push back a small amount of the parafilm wall to expose a tiny part of the conductive side of the slide.
15. Place the multimeter probes on opposite ends of the solar cell's conductive glass slides.



16. Place the solar cell under light, using either sunlight or a flashlight.
17. With the multimeter set to measure electric potential, measure the voltage of the solar cell.

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Introduction and Background – Ensuring a Uniform Level of Understanding while Engaging the Audience[2,3,4]

Below are a few things you'll probably want to mention as you introduce your demonstration. Again, it's not necessary to include all the details but to make sure the audience follows what you're showing them and why it's important. Keep the extra stuff in the back of your mind for answering questions or prompting discussion. Have a few questions (and answers) prepared to ask the audience in case they don't come up with any.

What is green chemistry?

(see page 2 of this packet and http://www.acs.org/content/acs/en/greenchemistry.html)

What is Solar Energy?

Solar energy is the energy given off by the sun. Because it is free and abundant, solar energy is a viable alternative to petroleum-based fuels. The amount of energy contained in the sunlight that reaches Earth every hour could meet a year's worth of global energy demand. However, about 30% is reflected back to space and approximately 50% becomes heat energy. The amount of sunlight that reaches a particular spot on Earth varies greatly due to the time of day, weather conditions, and location. Solar energy can be converted into electricity with a solar cell, also known as a *photovoltaic cell*. Photovoltaic cells have traditionally been expensive and relatively inefficient (compared to other forms of energy generation). In this demonstration a cell known as a dye-sensitized solar cell (DSSC) is constructed.

What is a DSSC and how does it work?

DSSC's are units that convert solar energy into electrical energy. They work as a result of reduction-oxidation (redox) chemistry that occurs in the nanocrystalline structure of titanium dioxide (TiO_2).

Depending on your audience, you may need to define reduction and oxidation. Recall that reduction is when a chemical species gains electrons and oxidation is when a chemical species loses electrons. Electrical currents are generated through redox chemistry; electrons move when one substance loses an electron and another substance gains an electron. As with people playing musical

[2] Hill, J.W., McCreary T.W., Kolb, D.K. (2012) *Chemistry for Changing Times*: Prentice Hall.
[3] Middlecamp, Catherine, ed. Chemistry in Context: Applying Chemistry to Society. 8th ed. New York: McGraw Hill, 2014. Print
[4] http://www.esf.edu/

chairs where when one person leaves a seat empty another fills it, a steady current is achieved as electron flow between chemical species generates electricity.

This is a great video of the chemical processes that occur: http://www.youtube.com/watch?v=3KRHJSOgzcw . (The key differences between the cell shown in this video and the one you'll be constructing for the demonstration are that you will not require a precious metal such as platinum or ruthenium , the conducting material spread on the second electrode for the demonstration is carbon from a graphite pencil, you will not soak your slide in the dye overnight , only for 3-5 minutes, and you will not need to heat up your cell.)

What are the materials used and their potential health and environmental impacts?

Titanium dioxide (TiO_2) is a common ingredient in a variety of products such as paints, lotions, and food coloring as well as processes such as wastewater treatment. It is a bright white powder and can be produced as a nanomaterial meaning it is designed, manipulated, and manufactured on the nano-scale (1 nanometer is about 100,000 times the width of a human hair). The white (thus not very light-absorbent) titanium dioxide nanoparticles bind to anthocyanins from the blackberry juice during dying which "sensitizes" the TiO_2 to light by making it darker and more light-absorbent. It also acts as the semi-conductor in the cell meaning it is the material through which electrons pass as they generate current.

There is concern about TiO_2's property of becoming activated by sunlight and catalyzing reactions that are toxic to aquatic life. This has led to discussions of whether or not its use in consumer products will impact the environment.[5] Titanium dioxide manufacture can result in sulfur-compound emissions (SO_x, free sulphuric acid, metallic sulphates) and chlorine compound emissions (free hydrochloric acid and metallic chlorides). Greening of the titanium dioxide production process has, however, been underway in Europe since the 1970's.[6]

Indium tin oxide (ITO) is a yellowish alloy (combination) of indium oxide and tin oxide powders that are mixed and compacted. It has many applications including liquid crystal displays (LCD screens), energy-saving windows, and as a thin coating for touch-screens. A downside of ITO production is the amount of energy used to homogenize the two powders (heating at about 1500 degrees Celsius for multiple hours). Through modern production processes, a significant amount of ITO and waste from production is reclaimed.[7]

Potassium Iodide is a white salt, similar in structure to sodium chloride (table salt), which has a variety of therapeutic uses, such as for hyperthyroidism and for radiation protection. It is considered to have relatively low toxicity.[8]

Propylene Glycol is a colorless, odorless liquid that has many applications such as in food, laundry detergents, and inks. It is readily biodegradable and not toxic to aquatic life).[9] In addition, it can be made from glycerol, a byproduct of biodiesel production.

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[5] http://www.epa.gov/nanoscience/nano-research.htm#character

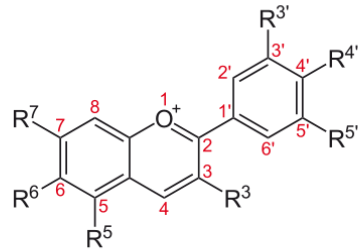
[6] "Council directive on procedures for harmonizing the programmes for the reduction and eventual elimination of pollution caused by waste from the titanium dioxide industry", *Official Journal of the European Communities*, 1993, http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:31992L0112&from=EN

[7] Chemical Information Profile for Indium Tin Oxide, *National Toxicology Program,* 2009 http://ntp.niehs.nih.gov/ntp/noms/support_docs/ito060309_508.pdf

[8] http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=4875#x291

[9] http://www.dow.com/productsafety/finder/prog.htm#HealthInfo

Anthocyanins are compounds responsible for the colors of fruits, vegetables, and autumn leaves. They are an essential part of the DSSC constructed in this demonstration because they bind to (dye) the TiO_2 a dark purple which allows it to absorb light.



Anthocyanin (Wikimedia Commons)

Talking Nerdy – Information to Help Keep the Presentation Green Chemistry-Focused
(The good, the bad, and the things researchers are trying to improve)

The information and questions below address how the demonstration relates to the principles of green chemistry while showing the need for further research which might be inspiring for members of the audience. Consider how you can craft your talk to motivate those listening to share what they've learned and pursue further information.

Do the costs of generating renewable energy outweigh the benefits?[10]

An important note to make on the subject of renewable fuels is that, while the current processes and products have faults, they still play major roles as steps in a general movement towards sustainability. In addition, note that many industrial-scale bio-processes, such as the use of lignocellulosic material to create fuel, are still in the early phases of development and won't necessarily be as efficient as something like the petrochemical industry's processes which have been evolving since the 19th century.

Industrial processes require large amounts of energy and fossil fuels have long been the standard for meeting these demands due to their relatively high energy output and low cost. However, these materials are non-renewable, the energy cost to extract them from the earth is high, and they release greenhouse gases when burned that would otherwise remain stored in the earth. According to the U.S. EPA, "Fossil fuel-fired power plants are responsible for 70 percent of the nation's sulfur dioxide emissions, 13 percent of nitrogen oxide emissions, and 40 percent of carbon dioxide emissions from the combustion of fossil fuels. These emissions can lead to smog, acid rain, and haze." Such processes as mining, drilling, and hydraulic fracturing for extraction of non-renewable resources do not return safe substances to the environment as would be preferred for a green chemistry process, but rather they input materials known to be hazardous to ecosystems and which might pollute ground water.

Solar energy has advantages over non-renewables. For example, when generating energy, solar panels do not have emissions and transporting solar panels is less risky than transporting oil. Generating energy from renewable resources is, of course, not without its problems. In some cases, the manufacture and disposal of photovoltaic cells requires more energy than the cells will ever produce. In addition, some scarce elements are frequently used in photovoltaic cells, such as cadmium which is highly toxic and creates difficult to manage waste. The amount of land needed for solar farms is also a concern, but it has been proposed that areas such as deserts, which have no agricultural value, could be utilized. Although these environmental impacts of solar energy are not of the same magnitude as those

[10] Jimenez-Gonzalez, C., Constable, D. J. C. (2011) *Green Chemistry and Engineering: A Practical Design Approach.* Hoboken, New Jersey: John Wiley & Sons, Inc. pp.613-630

caused by non-renewables the cost of solar power is not yet competitive on a large scale for the problems it does create.

How promising are newer alternatives to traditional solar cells?

The DSSC in this demonstration will probably only provide around 300 millivolts of energy. Someone in the audience may point out that this is very little compared to the 120 volts provided by a standard wall outlet, i.e. not enough to seem useful. This is an opportunity to discuss solar farms, the amount of energy they are currently able to provide and to transition into the research being conducted.

"Traditional" solar panels and their chemical components are inefficient and environmentally unfriendly compared to what recent research has produced. Alternatives, such as tin, show potential for replacing toxic elements like cadmium and other toxic or endangered elements in solar panels. See MIT's technology review for a few examples of how solar cells are being improved.

What is "benign by design" and how does it relate to renewable fuel sources?

The phrase "benign by design" for green chemistry is the goal that for every step of an item or material's creation and use little or no risk to the environment, human health or safety is posed because the processes and materials involved were carefully considered. Research is being done to provide solar cells that are not hazardous to the environment at any point in their life cycle. *Life cycle* refers to the consecutive and interlinked stages of a product or service system from the extraction to natural resources to the final disposal. *Life cycle assessments* are conducted to evaluate the potential risks to human and environmental health.

Bioprocesses for renewable energy have been explored. Biotechnology is a promising direction to look for answers to the search for cleaner, more efficient processes not only in energy production but for a wide range of chemical systems. Fuel cells and hydrogen-producing algae are just two bio-based technologies.

Consider that propylene glycol is used here instead of ethylene glycol as a very easy replacement. In addition, rather than using synthesized anthocyanin or a chemical dye, a fresh blackberry – obviously renewable, non-toxic, and biodegradable - was squished for this demonstration. Even slight changes to existing processes, often called "drop-in" technologies, can significantly improve safety and reduce the environmental impact. One well-known example of better design in action is the synthesis of ibuprofen, which you can learn about here and more technically, here.

Since we're already set up to use them, isn't there any way to make using fossil fuels "greener"?

Although there have been advancements in industries such as coal-fired power plants through emissions filtration technologies, for example, there are still hazardous byproducts that must be treated or disposed of such as mercury and sulphur dioxide. In the big scheme of things, fossil fuels eventually run out. Their eventual scarcity could result in an unstable economy through price volatility as critical metals like indium exhibit now. Why depend on a limited resource with inherent risks when innovation for renewable energy is ever-increasing in efficiency and associated hazards are reduced?

How does it impact members of the audience? (i.e. the "so what?" of your presentation)

Although we often treat resources like petroleum and precious metals as if they are unlimited they are, in fact, finite and often environmentally and socially costly as well as dangerous to extract. There are countless ways in which chemical practices affect everyone and those effects are likely to be negative if left unchecked. Numerous government agencies and independent private regulatory/certification groups around the world try to protect consumers, workers, and the planet by encouraging innovation and enforcing regulations based in green chemistry.

Without green chemistry the earth and its inhabitants are likely to experience more chemical disasters, polluted water, increased risk of cancer and disease, and to face a shortage of critical resources (everything from fuel to food and from clean air to materials needed for cell phones). Current chemical practices are often not sustainable enough to continue providing the standard of living many people have come to expect.

See Appendix A for specific examples.

Additional Resources

Example Questions and Prompts for the Audience

- *“What do you think about solar energy? About renewable energy in general?”*
- *“Does anyone have solar cells on their home?”*
- *“What do you think goes into producing a typical solar cell? Are they really better for the environment?”*
- *“What principles of green chemistry (as discussed in the introduction) apply to solar cells”*

Suggested Visual

If you’re able to get ahold of the materials it’s very easy to set up a “self-powered light bulb.” You need a solar panel, alligator clips, a flashlight and a bulb. Check out this video.

Or when practicing your demonstration see if you’re able to light a very small bulb with the cell (or a series of several) you constructed. If it works, show it to the audience during the presentation.

Video of Solar Cell Assembly from Beyond Benign

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Extraction of d-Limonene with Supercritical CO_2

(adapted from Beyond Benign)

This is a quick and easy demo that is connected to a variety of important green chemistry topics. Because essential oils from fruits and vegetables are found in a range of products such as cosmetics, food, medicine, and cleaning supplies there are many ways in which the demonstration is relevant to a general audience. In addition, little set-up is required and the audience can take home their own d-limonene-infused cleaning product.

Materials

-oven mitts
-2 oranges
-grater; zester
-2 weigh boats
-balance
-spatula
-5 15mL polypropylene centrifuge tubes with caps (Corning Catalog #430052). Do not re-use the tubes more than three times. *Do not substitute these with another type of tube as shattering of alternative vessels is dangerous. Be aware that the cap may pop off due to pressure build-up. Be sure the cap is not stripped (discard if it is) and that it is screwed on as tightly as possible.*
-100mL or larger plastic graduated cylinder or acrylic hydrometer cylinder (clear tubes increase the visual effect during a demonstration)
-1 lb dry ice in an ice bucket
-Kimwipes
-tweezers

Procedure

1. Put on safety gloves and glasses.
2. Fill plastic cylinder with about 70mL room temperature water

3. Using the grater or zester on only the colored part of the orange peel to collect 1 grams in a weigh boat.
4. Place the 1 gram of orange peel onto a kimwipe and make a small bundle so no material can escape.
5. Place the kimwipe bundle into the polypropylene centrifuge tube and use the spatula to push the peel toward the bottom of the tube but not into the conical end.
6. Wearing the oven mitts and working quickly, crush the dry ice into very fine pieces using a mortar and pestle. Finer is better.
7. Fill the centrifuge tube to the top with freshly, finely crushed dry ice. Tap the bottom of the tube against the counter or lab bench to pack as much dry ice in as possible.
8. Place the cap on the centrifuge tube and tighten carefully. Make sure the seal is tight but don't over tighten or the cap will become loose again.
9. Place the tube in the water in the graduated cylinder. Stand back from the tube as the reaction begins. A hissing noise may come from the tube as carbon dioxide escapes. This observation should be followed by the liquid CO_2 forming and bubbling inside the tube. *Do not attempt to remove the tube from the graduated cylinder while there is liquid CO_2 because it is under pressure and may rupture.*
10. Allow the reaction to continue until all the liquid CO_2 stops bubbling and disappears.
    a. Note: if the solid dry ice shrinks in diameter the experiment needs to be redone. The dry ice level should get lower but stay the same thickness.
11. Remove the tube from the water and slowly uncap it. Always point the tube away from your face and body.
12. Add more crushed dry ice and repeat the process a few times until you can see a pale yellow liquid at the bottom tip of the centrifuge tube. This is the d-limonene essential oil.
13. Carefully remove the kimwipe bundle trap using tweezers. Keep the tube upright to avoid any loss of the oil. The only thing in the tube should be d-limonene.
14. The tube can be passed around for members of the audience to observe the orange scent.

Interactivity: To give members of the audience something to take home consider extracting extra d-limonene the day before in your lab and mixing it with hand sanitizer. Divide the hand sanitizer into travel-size bottles for attendees to take home.

Safety Notes

- Do not use glass during this demonstration. Use only the recommended tube for containing the reaction.
- Be sure to wear goggles and that nothing is placed above the plastic cylinder
- Handling dry ice without gloves can cause skin damage so be sure to wear gloves
- Stripped caps should be discarded and replaced (these are caps that cannot be completely tightened and just continue to turn)

Introduction and Background – Ensuring a Uniform Level of Understanding While Engaging the Audience

Below are a few things you'll probably want to mention as you introduce your demonstration. Again, it's not necessary to include all the details but to make sure the audience follows what you're showing them and why it's important. Keep the extra stuff in the back of your mind for answering questions or prompting discussion. Have a few questions (and answers) prepared to ask the audience in case they don't come up with any.

What is green chemistry?

(see page 2 of this packet and http://www.acs.org/content/acs/en/greenchemistry.html)

What's going on with the bubbles and where does the dry ice go?

During the essential oil extraction, three physical states of carbon dioxide – solid, liquid, and gas - can be observed simultaneously. The bubbles observed in the tube of dry ice during this extraction are the result of the pressure change. Normally, dry ice sublimes, meaning it changes directly from a solid to a gas. However, due to its confinement in the tube the pressure increases, the liquid state is observed and bubbles form as the liquid turns into a gas which escapes from the tube.

What is a supercritical fluid?[11]

A supercritical fluid is a material in the physical state beyond its "critical point," i.e. when it is at too high a temperature and pressure to be classified as either a liquid or a gas. This state is sometimes called a dense gas. Higher densities are proportional to better solvating power meaning that supercritical CO_2 is competitive as a green solvent and can dissolve soils making it an effective cleaner. Common supercritical solvents include water, methane, n-pentane, and methanol. Carbon dioxide, however, has promising "green" applications as it has very low toxicity, is non-flammable, recyclable and inexpensive. Carbon dioxide has the added benefit of having a relatively low critical temperature and pressure. Therefore, producing supercritical CO_2 has a relatively low energy cost for use in industrial processes.

This experiment uses liquid CO_2 in place of supercritical CO_2 because reaching the supercritical point of carbon dioxide is not feasible for a demonstration. However, liquid CO_2 has also been used in industrial processes in place of more hazardous solvents, particularly for greener dry cleaning (see

[11] Anastas, P.T., Williamson T.C. (1998) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes.* Oxford, United Kingdom: Oxford University Press. pp.312-333.

Appendix A). Carbon dioxide's toxicity is low enough that it is considered safe for workers to be exposed to it day after day without a risk to their health.[12]

Isn't carbon dioxide bad for the environment?

Carbon Dioxide (CO_2) gas comes from natural and anthropogenic sources such as breath exhalation and the burning of fossil fuels, respectively. While carbon dioxide emissions from burning fossil fuels such as coal are considered a greenhouse gas, CO_2 in the form of a supercritical fluid is inherently not emitted into the atmosphere. CO_2 for use as a solvent is sequestered out of the atmosphere thus having no effect on the net amount in the air. Many processes that use supercritical CO_2 also re-use it in closed-loop systems. Additionally, the reduction of occupational hazards and hazardous waste from using supercritical CO_2 in place of toxic substances ensure that its overall impact is relatively low. The transportation of volatile, toxic compounds like arsine and phosphine normally used in processes such as aerosolization is also avoided.[13]

What is d-Limonene, what is it used for, and why can't you just squeeze it out of citrus rinds?

D-Limonene is an essential oil found in the rinds of citrus peels. Chemically classified as a *monocyclic monoterpene* it is a major component of the flavor and fragrance of citrus fruits like oranges, lemons, and grapefruit. It is GRAS, or Generally Recognized as Safe by the U.S. Food and Drug Administration, meaning it has relatively low toxicity. One estimate found that the average American consumes about 16mg of d-Limonene a day through citrus fruit consumption.[14]

D-Limonene is used in a variety of consumer goods for its cleaning (degreasing) capability and pleasant odor. These include things like detergents, shampoos, cosmetics, and flavor enhancers for everything from ice cream to baked goods. It has also been used in a few medical applications such as breaking up gallstones and as part of cancer treatment.[15] D-Limonene is also a less hazardous solvent that can be used in place of halogenated chemicals (some of which can deplete the ozone layer) or those with health risks, like n-Hexane (known to affect the nervous system). Some manufacturers of d-limonene use the byproducts of orange juice manufacture to make the chemical, thus minimizing waste.

There are many chemicals in the rinds of citrus fruits so squeezing the fruit would not give a purified essential oil. Other compounds in the mixture that would leach out of the orange include carotenoid pigments (the color of the rind) and vitamins.[16]

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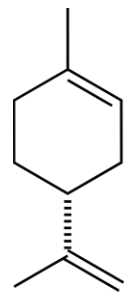
[12] Soares, V. B., & Coelho, G. L. V. (2012). Safety study of an experimental apparatus for extraction with supercritical CO_2. *Braz. J. Chem. Eng.*, *29*(3), 677-682. August 06, 2014. http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0104-66322012000300023&lng=en&tlng=en. 10.1590/S0104-66322012000300023

[13] Anastas, P.T., Williamson T.C. (1998) Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes. Oxford, United Kingdom: Oxford University Press. pp.317-318.

[14] Hakim, I.A., Harris R.B. and Ritenbaugh C. (2000) Citrus peel use is associated with reduced risk of squamous cell carcinoma of the skin. *Nutrition and Cancer*. 37(2), 161-168. http://69.164.208.4/files/Citrus%20Peel%20Use%20Is%20Associated%20With%20Reduced%20Risk%20of%20Squamous%20Cell%20Carcinoma%20of%20the%20Skin.pdf

[15] Sun, Jidong (2007) D-Limonene: Safety and Clinical Applications. *Altern. Med. Rev.* 12(3), 259-264. http://www.anaturalhealingcenter.com/documents/Thorne/articles/Limonene12-3.pdf

[16] Glenn, J.H. (1957) Chemistry of Citrus Fruits. *J. Chem. Educ.* 34(10), 513-516. http://pubs.acs.org/doi/pdf/10.1021/ed034p513



D-Limonene, source: Wikimedia Commons

What else can supercritical CO_2 be used for?

Supercritical CO_2 already serves a variety of functions and research is being done for further applications. Decaffeination of coffee beans can be done with supercritical carbon dioxide: the CO_2 removes the caffeine which is then transported by water as a high-concentration solution that can be sold to soft-drink manufacturers while the CO_2 itself is re-used for further caffeine extractions.[17] Supercritical CO_2 used for aerosolization as an alternative to electroplating which generates hazardous liquid waste or as an alternative to halogenated or oxidant-forming compounds which are also a risk to the environment and pose an occupational hazard. Aerosols are widely used in the pharmaceutical industry for drug delivery and for making thin films like touch screens.[18] Supercritical fluids are currently a popular area of research and new applications are in development.

Green Chemistry Topics to Emphasize for this Demonstration (adapted from Beyond Benign)

[17] Jimenez-Gonzalez, C., Constable, D. J. C. (2011) *Green Chemistry and Engineering: A Practical Design Approach.* Hoboken, New Jersey: John Wiley & Sons, Inc. p.154

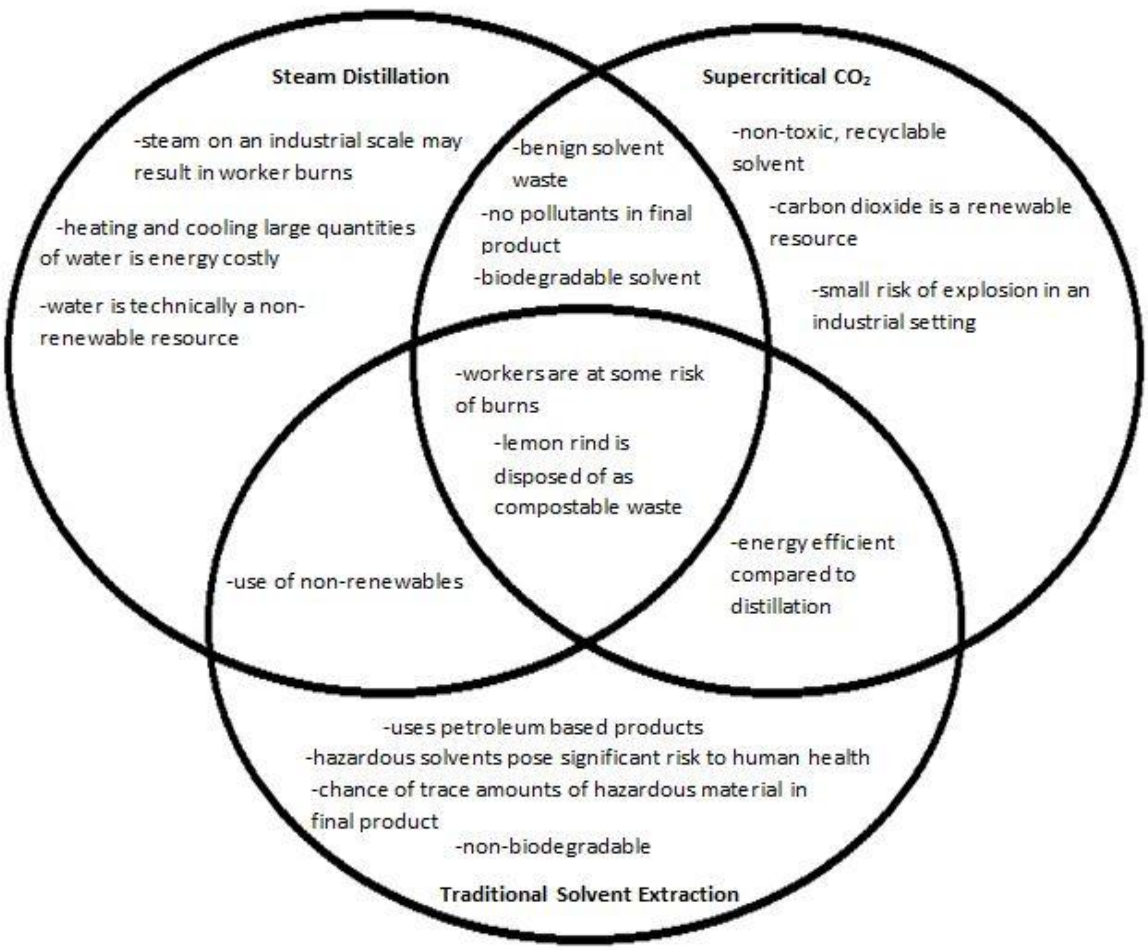
[18] Anastas, P.T., Williamson T.C. (1998) *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes.* Oxford, United Kingdom: Oxford University Press. pp.312-314.

Use of renewable resources, avoiding waste, returning safe substances to the environment, conserving energy and getting off to a safe start are all relevant green chemistry topics in the context of this demonstration. The Venn-diagram below shows how green chemistry principles apply to each method of essential oil extraction.

Additional Resources

Example Questions and Prompts for the Audience

- *"Why not just provide workers with proper protection from chemicals and treat the waste responsibly?"*
    - A response to this could be another question: why put people in harm's way at all if it can be avoided? Protection equipment can be costly and may not be used consistently or correctly. Processes should be designed to prevent harm to human health and the environment. In addition, even if hazardous waste can be treated or recycled this often involves additional energy use and transportation of hazardous materials to processing facilities which increases the risk of chemical release to the



environment. Something else to note: nothing is ever really thrown away. How likely is it that a manufacturer will thoroughly investigate where the hazardous waste stream goes and how it is really treated?

- *"Why might the use of supercritical carbon dioxide on an industrial scale pose a human health risk? Does this risk outweigh the benefits?"*
    - Even in this small-scale demonstration there is a risk of the polypropylene tube's cap flying off and causing an injury. Any material stored and used at a high pressure is an important engineering consideration. Damage to equipment, workers, and the environment are considered when modelling potential industrial accidents. One study found that the risk of worker eardrum injury from explosion was more concerning that of death from machine fragments or lung injury and headsets were therefore recommended. Development of stronger vessels for extraction liquids is also underway as more is learned about high-pressure materials.[19]
- *"Why is the use of water in steam distillation problematic if it's non-toxic and works well? What if the energy used to heat and cool the water was from a renewable source such as solar power?"*
    - Although it is non-toxic and biodegradable water is not unlimited and as an essential resource that fulfills many, many other needs an extraction process that uses steam distillation is inherently not designed as well as one that does not even if it is heated and cooled with renewable energy.
- *"What principles of green chemistry (as discussed in the introduction) apply to this demonstration?"*
    - See Venn-diagram above.

Here is a video of a similar procedure from the University of South Hampton.

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Bio-Diesel Demonstration

(adapted from Beyond Benign)

Making bio-diesel is surprisingly simple and touches on a number of green chemistry topics such as using renewable resources, designing less hazardous chemical syntheses, using safer solvents, and returning safe substances to the environment.

Materials

20 mL of ethanol (CH_3CH_2OH)
0.35 g sodium hydroxide (NaOH)
20 mL of vegetable oil
125 mL Erlenmeyer flask
magnetic stir bar
stir/hot combination plate
balance or scale
weigh paper or weigh boat
spatula or scoopula

[19] Soares V.B., Coehlo G.L.V., Safety Study of an Experimental Apparatus for Extraction with Supercritical CO_2. *Braz. J. Chem. Eng.,* 2012, 29(3), pp.677-682. http://www.scielo.br/pdf/bjce/v29n3/23.pdf

50 mL graduated cylinder
thermometer capable of measuring 40˚C

Procedure

Because this synthesis of biodiesel would normally be done in a two-part lab and the reaction mixture would be allowed to sit overnight you'll have to do the synthesis twice: once in a lab before the demonstration to have a fully prepared example and once during the actual demonstration. This way, rather than making the audience sit around overnight you'll simply go through all the synthetic steps during the demonstration and then pull out the completed biodiesel that you made the day before. Think of any cooking show you've ever watched in which there's a meal that's ready to come out of the oven just when the celebrity chef finishes assembling their dish step-by-step for the viewer.

1. Wear safety goggles, gloves and apron.
2. Measure 20 mL ethanol in the 50 mL graduated cylinder.
3. Transfer the ethanol into the 125 mL Erlenmeyer flask.
4. Add a magnetic stir bar into the flask.
5. Place the flask on a stir/hot plate and turn on the stir function on the stir/hot plate. Stir the ethanol at a medium speed.
6. Using weigh paper (or a weigh boat) and a spatula (or a scoopula), measure 0.35 g of NaOH on a balance.
7. Transfer the NaOH into the flask. Allow the solution to stir until all of the NaOH has dissolved. *Sodium ethoxide has formed inside the flask.*
8. Measure 20 mL of vegetable oil using the graduated cylinder.
9. Transfer the vegetable oil into the flask.
10. Turn on the heat function of the stir/hot plate and allow the vegetable oil to warm to 40ºC.
11. Heat and stir the mixture at 40˚C for 30 minutes.
12. Turn off the stir/hot plate and remove the flask from the top of it.
13. Allow the mixture to sit in the test tube rack overnight to separate into 2 layers: biodiesel and glycerol. Glycerol has a higher density than biodiesel and will therefore constitute the layer at the bottom of the test tubes.
14. Repeat this procedure (except step 13, of course) in front of the audience. Then, once all ingredients have been mixed reveal the separated mixture from the day before.

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What is green chemistry?

(see page 2 of this packet and http://www.acs.org/content/acs/en/greenchemistry.html)

What are biofuels?

Biofuels are any fuel derived from natural sources such as agricultural products. Ethanol and biodiesel are the two major categories of biofuels with ethanol being created from a sugary feedstock (like corn or sugarcane) and biodiesel is based on plant oils (like canola or peanut). Biofuels are created with the intention of substituting a fossil fuel like oil or coal. First generation biofuels are created from "new" plant materials while second generation biofuels are created from the waste byproducts of plant processing industries.[20]

Are sodium hydroxide and sodium ethoxide safe and environmentally friendly?

Sodium hydroxide (NaOH) is used in this reaction as a catalyst in the transesterification reaction of a triglyceride to three biodiesel molecules and the glycerol byproduct. Triglycerides are compounds found in oils that when converted into large biodiesel molecules (the process called transesterification) have many bonds available to break.[21] The breaking of chemical bonds is what produces energy during combustion.

Sodium hydroxide is a basic, white solid, also known as lye, which has long been used in the manufacture of soap. In its concentrated form or large doses it poses health risks such as lung inflammation if inhaled or burns on the skin. It is not, however, considered to cause cancer, genetic mutations or have reproductive effects.[22] It is a common household cleaning chemical and you can even order it online. In industry, sodium hydroxide is often used to neutralize the pH of wastewater and therefore has a lower risk of affecting the pH of waterways. On the other hand, the U.S. EPA requires that sodium hydroxide products such as pesticides must state that they are toxic to wildlife and are not to be discharged into any bodies of water without registration and analysis.[23]

Sodium ethoxide (C_2H_5ONa) is a white or yellow powder that forms as a byproduct when the NaOH catalyst is added to the warm ethanol. Its production would be an inherent risk on an industrial scale because of its flammability and reactivity with water and risk of skin and lung burns from exposure. The National Institute for Occupational Safety and Health (NIOSH) does not note any long term health effects such as carcinogenicity or nontoxicity.[24] In a waste stream on an industrial scale, sodium ethoxide is easily treatable according to the EPA because it does not form an "unstable, air and water reactive solid."[25]

What is glycerol and is it a useful byproduct?

Glycerol ($C_3H_5(OH)_3$) has traditionally been used as an ingredient in soap and is considered non-toxic. A simple catalytic synthesis developed by the 2006 recipients of a Presidential Green Chemistry Challenge Award changing glycerol to propylene glycol ($C_3H_6(OH)_2$) has reduced the amount of waste from the biodiesel production process. The complimentary nature of two green chemistry principles, catalyst use and waste reduction, is exemplified here. Rather than simply discarding this byproduct - which is generated in a 1:9 ratio with biodiesel - a copper catalyst is an efficient way to convert a waste product into an U.S. FDA approved material that is used in many consumer goods including soaps, ice cream, and paints. This not only avoids waste generated through the conventional process but in

[20] http://ec.europa.eu/energy/renewables/studies/doc/land_use_change/study_jrc_biofuel_target_iluc.pdf
[21] Lange, Marty (ed.) (2012) *Chemistry in Context* New York, N.Y.: McGraw Hill, p.187
[22] http://www.hpa.org.uk/
[23] http://www.epa.gov/oppsrrd1/REDs/factsheets/4065fact.pdf
[24] http://www.cdc.gov/niosh/ipcsneng/neng0674.html
[25] http://www.epa.gov/superfund/sites/rods/fulltext/r0388054.pdf

addition lowers the price of biodiesel as glycerol and propylene glycol can be sold by fuel manufacturers.[26]

What's the point of making renewable fuels?

An important note to make on the subject of renewable fuels is that, while the current processes and products have faults, they still play major roles as steps in a general movement towards sustainability. In addition, note that many industrial-scale bio-processes, such as the use of lignocellulosic material to create fuel, are still in the early phases of development and necessarily won't be as efficient as something like the petrochemical industry's processes which have been evolving since the 19th century. Industrial processes require large amounts of energy and fossil fuels have long been the standard for meeting these demands due to their relatively high energy output and low cost.

The availability of fossil fuels is limited due to their sources: they take millions of years and specific geologic conditions to form and are often geographically challenging to extract because of physical and/or political obstacles. This results in price volatility and a lack of guarantee of a continual supply. Biomass, the source material for biofuel, can be grown domestically and comes in many forms like corn, switch grass, bamboo, soybeans, and more. According to the U.S. EPA, "Fossil fuel-fired power plants are responsible for 70 percent of the nation's sulfur dioxide emissions, 13 percent of nitrogen oxide emissions, and 40 percent of carbon dioxide emissions from the combustion of fossil fuels. These emissions can lead to smog, acid rain, and haze." Such processes as mining, drilling, and hydraulic fracturing for extraction of non-renewable resources do not return safe substances to the environment as would be preferred for a green chemistry process, but rather they input materials known to be hazardous to ecosystems and which might pollute ground water.

There is controversy over whether or not biofuels are "worth it." Concerns about arable land use, production costs, efficiency, and pesticide and herbicide use are often raised. Although biofuels produce carbon dioxide when burned, their net contribution is much smaller than that of fossil fuels because the plants they are made from absorb carbon dioxide during their life cycle and would release it naturally when decaying (unlike fossil fuels in which the carbon dioxide would normally remain trapped and which do not produce oxygen). Biodiesel has the additional advantages of being non-toxic, biodegradable, and burning it does not release sulfur compounds[27].

Is it feasible to produce biofuels on a large scale?

The use of a catalyst in this process (like sodium hydroxide) on a large scale has environmental downsides as the purification of biodiesel requires washing with soap, salt, and lots of water which becomes waste.[28] However, research into more environmentally friendly methods has been done with some success including the use of supercritical fluids for transesterification.[29] The catalytic conversion of glycerol to propylene glycol was also an important step in creating more efficient biofuels.

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[26] Lange, Marty (ed.) (2012) *Chemistry in Context* New York, N.Y.: McGraw Hill, p.188

[27] Luque, R. Herrero-Davila, L, Campel, J.M, Clark J.H, Hidalgo, J.M., Luna, D., Marinas, J.M., Romero, A.A. Biofuels: a technological perspective. *Energy Environ Sci.,* 2008, 1, 542-564. http://pubs.rsc.org/en/content/articlepdf/2008/EE/B807094F

[28] *Ibid*.

[29] *Ibid.*

The prices of biomass would necessarily fluctuate with the seasons but presumably in a regular manner as opposed to the unpredictable changes in crude oil prices[30].

On the other hand, the refining of fossil fuels on an industrial scale has downsides that biodiesel refineries don't face. Hydrocarbon (fossil fuel) refining requires the addition of oxygen when biobases usually do not. This oxygenation is conventionally done through the addition of excess (stoichiometric) toxic reagents like lead and chromium which generates large amounts of hazardous waste[31].

The amount of land required to make biofuels remains a concern but some potential feedstocks are able to grow on land where agricultural products will not and the development of second-generation biofuels based on agricultural waste is rapidly expanding.[32]

There are many pros and cons to biofuel production some more of which are examined by the European Union Commission Institute for Prospective Technological Studies here. Again, keep in mind that this is a young industry where progress is being made through green chemistry and innovation.

Why choose ethanol rather than methanol?

Safer solvent selection is one of the 12 principles of green chemistry. Although ethanol and methanol are very, very similar in chemical composition there are some differences in their manufacture and associated risks that resulted in the choice to suggest ethanol over methanol in this experiment. Methanol is more toxic to humans than ethanol, for starters. The median lethal dose of pure methanol in rats in about 20 times higher than the LD50 of pure ethanol suggesting that the health hazards for humans dealing with methanol is much greater as well.[33,34]

In addition to health risks, the methanol is often produced by burning fossil fuels to collect the methane from which it is derived. Producing methanol without the use of fossil fuels is rarely cost-effective or practical and methanol has a lower energy density than gasoline anyway, so more of it is needed despite being cheaper by the gallon.[35]

What's the deal with volatile organic compounds (VOCs)?

Volatile organic compounds are chemicals which are likely to become airborne through evaporation. VOCs can be problematic both indoors and outdoors. All indoor compounds that evaporate from paints, furniture, etc. are considered VOCs that should be assessed for their risk to human health while only certain chemicals which evaporate outdoors are regulated. The U.S. EPA states that, "For example, methylene chloride (paint stripper), and perchloroethylene (dry cleaning fluid), are exempted compounds for outdoor regulation, but they could pose serious health risks to exposed individuals if present indoors. The first is listed by the International Agency for Research on Cancer (IARC) as a potential human carcinogen and the second is listed as a probable human carcinogen. Indoor VOCs react with the indoor ozone even at concentrations below public health standards."

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30 Anastas, P.T., Williamson T.C. (1998) Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes. Oxford, United Kingdom: Oxford University Press. p.28

31 *Ibid.*

32 http://ec.europa.eu/energy/renewables/studies/doc/land_use_change/study_jrc_biofuel_target_iluc.pdf

33 http://kni.caltech.edu/facilities/msds/methanol.pdf

34 http://www.sciencelab.com/msds.php?msdsId=9923955

35 http://www.biofuelsdigest.com/bdigest/2010/05/24/methanol-biofuel-to-love-or-hate/

VOCs that are regulated by the U.S. EPA outdoors lead to tropospheric ozone production (low-level smog) through their reactions with nitrogen oxides.[36]

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Appendix A: Everyday Examples of Green Chemistry[37]

Below are some interesting examples of how green chemistry affects everyone.

- *Have you ever had you clothes dry-cleaned?*[38]
    - Dry Cleaning: dry-cleaning processes have conventionally used the chemical perchloroethylene (perc). Several organizations have stated that perc is a hazardous substance to human health. The International Agency for Research on Cancer (IARC) concluded that perc is a "probable human carcinogen" meaning it is likely to cause cancer in addition to its short term effects like dermatitis. Workers in a dry-cleaning facility can be exposed to perc in a number

[36] Jimenez-Gonzalez, C., Constable, D. J. C. (2011) *Green Chemistry and Engineering: A Practical Design Approach.* Hoboken, New Jersey: John Wiley & Sons, Inc. p.46

[37] http://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/examples.html

[38] Ryan, M. (ed.), Tinnesand, M. (ed.) (2002*) Introduction to Green Chemistry*, American Chemical Society: U.S.A. pp.23-29

of ways from cleaning the machine to simply loading clothing.[39] In addition, perc is categorized as a hazardous air pollutant by the U.S. EPA's Clean Air Act and it may contaminate groundwater when it is disposed.[40]
    - *Applying green chemistry to this situation has resulted in a markedly improved process using liquid carbon dioxide – a substance that is essentially non-toxic and is equally effective at removing grease and dirt from fabric. This simple innovation of replacing a hazardous chemical for a benign one is a perfect example of green chemistry at work in everyday life.*
- *Do you own something involving a computer chip?*
    - Have you ever considered what goes into making a smartphone, computer, or television work? As technology progresses so does our consumption of endangered elements: the 44 critical materials which will soon face supply limitations. These limitations can stem from factors such as geographic concentration, political motivations, regulatory laws, or consumer demand. Some green chemists are researching more abundant alternatives, more efficient syntheses where alternatives are not found, diversifying the supply and better recycling and recovery programs for these scarce materials. A smartphone, for example, usually contains over 80 elements, many of which are considered "endangered," for everything from the touch screen (dysprosium, europium, etc.) to the color display (yttrium, terbium, and more). To manufacture computer chips, many chemicals, large amounts of water, and energy are required. In a study conducted in 2003, the industrial estimate of chemicals and fossil fuels required to make a computer chip was a 630:1 ratio! That means it takes 630 times the weight of the chip in source materials just to make one chip! Compare that to the 2:1 ratio for the manufacture of an automobile. This is an example of very poor atom economy. Scientists at the Los Alamos National Laboratory have developed a process that uses supercritical carbon dioxide in one of the steps of chip preparation, and it significantly reduces the quantities of chemicals, energy, and water needed to produce chips. Richard Wool, director of the Affordable Composites from Renewable Sources (ACRES) program at the University of Delaware, found a way to use chicken feathers to make computer chips! The protein, keratin, in the feathers was used to make a fiber form that is both light and tough enough to withstand mechanical and thermal stresses. The result is feather-based printed circuit board that actually works at twice the speed of traditional circuit boards. Although this technology is still in the works for commercial purposes, the research has led to other uses of feathers as source material, including for biofuel.
- *Who owns clothes? By the looks of it, all of you!*
    - Micro-organisms are everywhere, even in our clothes. They cause odors, wearing, and color changes to fabrics in textiles. To reduce the number and effects of micro-organisms on our clothes, antimicrobial textiles have been developed. Unfortunately, some of these synthetic agents have toxic effects on humans. For example, silver antimicrobial agents have caused dermatitis, some synthetic dyes have been found to cause cancer, and still others like zinc pyrithione are mildly neurotoxic. Not only are

[39] https://www.osha.gov/dsg/guidance/perc.html
[40] http://yosemite.epa.gov/opa/admpress.nsf/0/e99fd55271ce029f852579a000624956

these compounds harmful to humans, they are often not biodegradable and the waste created by their manufacture is difficult to treat and sometimes become ineffective over time. *Green chemistry approaches have created benign antimicrobial textile solutions. These include materials called biopolymers that are made from a huge variety of renewable materials found in nature such as chitosan from crustaceans and fungi, cyclodextrin from starch, and alginate from brown sea weeds. Antimicrobial agents made from these ingredients are less harmful to the environment, have lower toxicity, are renewable, and still highly functional.* [41]

- *Have you ever eaten food?*

- Many people are surprised to learn that even what they eat is a product of chemical design. Decaffeination and the production of flavors are just two examples of food-industry processes that green chemistry principles have been applied to with success. Decaffeination of coffee beans using dichloromethane, a suspected carcinogen, was the accepted process for about 70 years. However, greener methods have been developed and applied on an industrial scale. The Swiss water process and the use of supercritical CO_2 are both the result of green chemical innovation. The Swiss water process uses water, green bean extract and a difference of caffeine concentrations. No harmful solvents are used and very little waste is produced as the water is easily recycled. Decaffeination by supercritical CO_2 is also a safer and more environmentally friendly method because it is a very low-waste process using a relatively non-toxic substance; the carbon dioxide is recycled throughout the process and the caffeine solution produced is sold to other manufacturers.[42]
- Consider everything vanilla-flavored you've ever eaten or vanilla-scented candles, soaps, and more that you've used. The production of synthetic vanillin, the main flavor component of natural vanilla extract, has undergone several changes through industry attempts to improve efficiency, reduce waste, and increase the quality as demand grows at a faster rate than vanilla bean production. In the 1930's, use ligninsulfonates (organic material from wood pulp production) became the conventional starting material for vanillin production but were eventually replaced by a petrochemical starting material due to the large amounts of waste created through the wood-production by-product process[43]. New research has found that vanillin molecules can be collected and purified using ionic solvents which are often greener than the solvents they replace (less volatile) and can be derived from renewable resources unlike petrochemicals[44]. Although this synthesis is still in development the pathway towards greener production is being paved.

- *Have you ever used plastic?*
  - Several companies have been working to develop plastics that are made from renewable, biodegradable sources.

[41] Shahid-ul-Islam, Shahid, M., Mohammad, F. Green chemistry approaches to develop antimicrobial textiles based on sustainable biopolymers – a review. *Ind. Eng. Chem. Res.* 2013, 52, 5245-5260.
[42] Jimenez-Gonzalez, C., Constable, D. J. C. (2011) *Green Chemistry and Engineering: A Practical Design Approach.* Hoboken, New Jersey: John Wiley & Sons, Inc.
[43] Calvo-Flores, F.G., Dobado, J.A. Lignin as a renewable raw material, *Chem Sus Chem.,* 2010, 3, 1227-1235. http://onlinelibrary.wiley.com/enhanced/doi/10.1002/cssc.201000157/
[44] http://www.sciencedirect.com/science/article/pii/S1383586610002789

  - NatureWorks of Minnetonka, Minnesota, makes food containers from a polymer called polylactic acid branded as Ingeo. The scientists at NatureWorks discovered a method where microorganisms convert cornstarch into a resin that is just as strong as the rigid petroleum-based plastic currently used for containers such as water bottles and yogurt pots. The company is working toward sourcing the raw material from agricultural waste.
  - BASF developed a compostable polyester film that called "Ecoflex®." They are making and marketing fully biodegradable bags, "Ecovio®,"made of this film along with cassava starch and calcium carbonate. Certified by the Biodegradable Products Institute, the bags completely disintegrate into water, CO_2, and biomass in industrial composting systems. The bags are tear-resistant, puncture-resistant, waterproof, printable and elastic. Using these bags in the place of conventional plastic bags, kitchen and yard waste will quickly degrade in municipal composting systems.
- *Have you ever taken a medication?*
  - Merck and Codexis developed a second-generation green synthesis of sitagliptin, the active ingredient in Januvia™, a treatment for type 2 diabetes. This collaboration lead to an enzymatic process that reduces waste, improves yield and safety, and eliminates the need for a metal catalyst. Early research suggests that the new biocatalysts will be useful in manufacturing other drugs as well.
  - Originally sold under the brand name Zocor®, the drug, Simvastatin, is a leading prescription for treating high cholesterol. The traditional multistep method to make this medication used large amounts of hazardous reagents and produced a large amount of toxic waste in the process. Professor Yi Tang, of the University of California, created a synthesis using an engineered enzyme and a low-cost feedstock. Codexis, a biocatalysis company, optimized both the enzyme and the chemical process. The result greatly reduces hazard and waste, is cost-effective, and meets the needs of customers.
- *Have you ever painted something?*
  - Oil-based "alkyd" paints give off large amounts of volatile organic compounds (VOCs). These volatile compounds evaporate from the paint as it dries and cures and many have one or more environmental impacts.
  - Procter & Gamble and Cook Composites and Polymers created a mixture of soya oil and sugar that replaces fossil-fuel-derived paint resins and solvents, cutting hazardous volatiles by 50 percent. Chempol® MPS paint formulations use these biobased Sefose® oils to replace petroleum-based solvents and create paint that is safer to use and produces less toxic waste.
  - Sherwin-Williams developed water-based acrylic alkyd paints with low VOCs that can be made from recycled soda bottle plastic (PET), acrylics, and soybean oil. These paints combine the performance benefits of alkyds and low VOC content of acrylics. In 2010, Sherwin-Williams manufactured enough of these new paints to eliminate over 800,000 pounds, or 362,874 kilograms of VOCs.

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Appendix B: Recommended Resources and Additional Labs

As with any subject there is bias among resources in chemistry. When giving a presentation and answering questions it's important to reference reliable sources in order to build the audience's confidence in your knowledge and credibility.

Keep an open mind when searching for answers. Consider viewpoints that oppose yours, whether or not they make claims based on facts, what organization has sponsored the research, and draw conclusions only after a review of a variety of credible sources.

The best places to find information are **peer-reviewed scientific journals**. Your university or college library will almost certainly provide free access to these articles. Email or visit your librarian if you're not sure how to get access (either online or in print). Google Scholar is a good place to keyword search for journal articles on the subject of interest.

There are a growing number of green chemistry **textbooks and lab manuals**. Again, your university or departmental library may have copies of these. Otherwise, you can always kindly request that the library order reference copies for chemistry students. A list of these textbooks can be found on the ACS Green Chemistry Institute website, here.

More and more **websites and databases** with information about green chemistry are popping up on the internet. For example, the Greener Education Materials for Chemists (GEMs) database provides a collection of green chemistry resources. The Nexus Blog from the Green Chemistry Institute is another source of articles and information on emerging science. The Washington State Department of Ecology has also put together a list of various online green chemistry resources.

A member of faculty in the chemistry department might be interested in green chemistry. Ask your chapter's advisor and inquire about current research at your university.

Be sure to **reference all material** used when generating media just as you would for a research paper even if you only expect the publication to circulate within campus.

Links and Ideas for Other Demonstrations

Your student chapter can apply the format of the above examples to other demonstrations. Consider ways in which what you're showing connects to green chemistry. How will your demonstration prompt the audience? What do you need to do to accurately inform them about green chemistry? More green chemistry labs can be found online such as at these websites Beyond Benign and The Berkeley Center for Green Chemistry and in the textbooks and lab manuals listed in Appendix B.

The American Chemical Society *Journal of Chemical Education* has exhibited many greened labs.

Submitting Your Green Student Chapter Activity

Once your ACS student chapter has completed a green activity it's time to fill out the student report with details about what's been done. Feel free to send along photographs or a mention of your work in the university or college news.

See this webpage for information on deadlines, submission requirements, and the report form.

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