The Green Chemistry Assistant: a new concept in web applications

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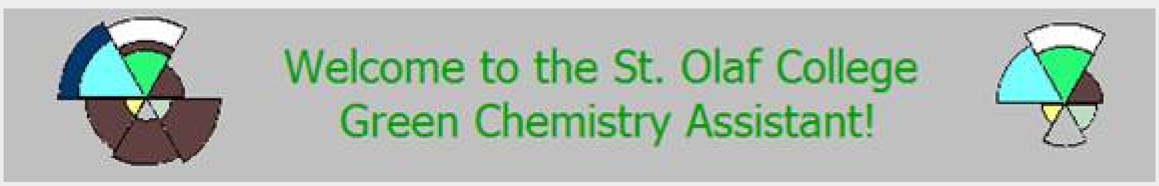
Abstract

The Green Chemistry Assistant (GCA), http://fusion.stolaf.edu/gca , is a collaborative project between St. OlafCollege and the U.S. Environmental Protection Agency that allows analysis of chemical equations, reactions, and processes in terms of green chemistry, safety, and chemical hazards. Geared toward a broad range of users, the site focuses on single- or multi-step processes for which the balanced chemical equations are known. Concepts such as atom economy, theoretical yield, experimental atom economy, process mass efficiency, and E-factor are explained and are calculated based on balanced chemical equations and experimental quantities introduced by users. In this paper, I will describe the capabilities of this "web application" (as opposed to a simple "web page" or "web site"), how we are using it at the undergraduate organic chemistry level, some of the surprises we have had both in terms of student capabilities and in terms of faculty expectations, and what it offers to the wider green chemistry community.

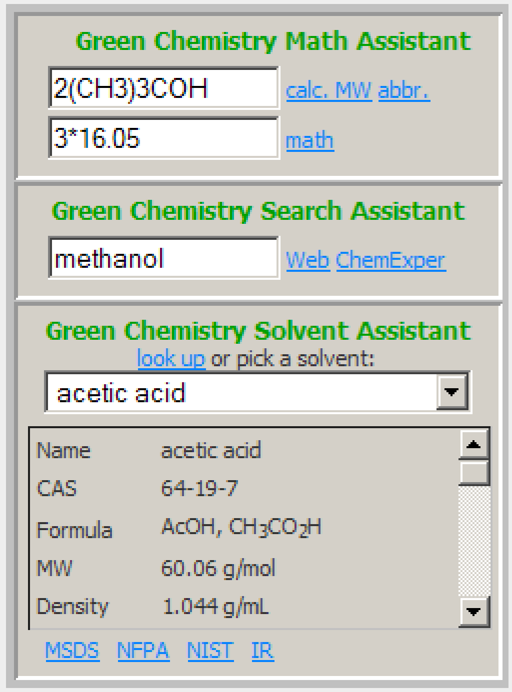


Introduction

Give a person a hammer, and they can build a house;

Give a person the ***idea*** *of a hammer,*

and they can build a better hammer.



The Green Chemistry Assistant (GCA) is simply a *tool*. It is just a site that allows a web-based analysis of chemical processes in terms of green chemistry measures --- theoretical yield, atom economy, process mass efficiency, E-factors, and the like. Being a tool, it is more similar to a glorified calculator than it is to awikipedia tutorial. Thus, a user should not expect a guided tour of green chemistry concepts here. Rather, a student or instructor or practicing research chemist in need of doing calculations relating to green chemistry might want to bookmark this site for those times when serious thought is being given to green chemistry analysis.

The three questions that I'd like to address in this paper in relation to the GCA include:

What sort of calculations would one want to do in relation to green chemistry?

How has having had easy access to these calculations changed our pedagogy?

What is the connection to laboratory safety and waste management?

I'll cut to the chase here: Students have learned that atom economy is just the tip of the iceberg. As faculty, we have learned that our students in organic chemistry are far less capable than we had initially imagined at being able to decipher a written reaction description. We have learned that green chemistry measures are far more subtly complicated than anyone generally makes them out to be. I have learned to appreciate the differences among the terms *equation*, *reaction*, and *process*, and I've learned how discussions relating to green chemistry can provide an accessible context for discussions of chemical safety and waste management.

What sort of calculations would one want to do in relation to green chemistry?

The obvious "first calculation" in green chemistry is atom economy. This much discussed term is simply the fraction of the mass of reactants that *theoretically* remains in the desired product after a chemical reaction:

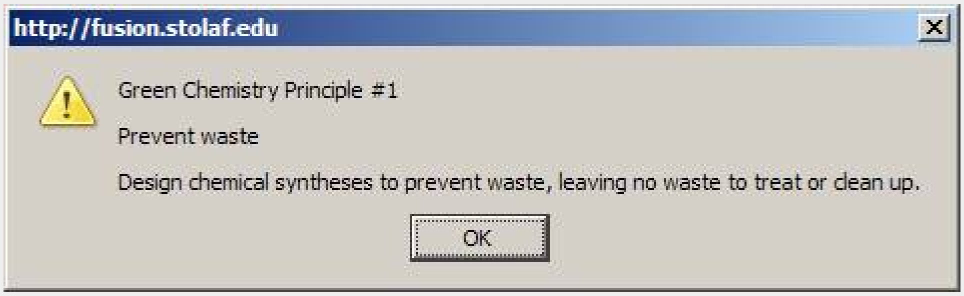
$$\textbf{Atom Economy} = \frac{\textbf{(desired product molar masses)}}{\textbf{(total reactant molar masses)}}$$

So this definition amounts to an expression of "desired output versus total input." We put X grams into a reaction; we get Y grams of our desired product out (theoretically). AE is just Y/X.

Interestingly, due to the law of mass balance, there is another equivalent way to conceptualize atom economy:

$$\textbf{Atom Economy} = \frac{\textbf{(desired product molar masses)}}{\textbf{(total product molar masses)}}$$

Here we focus entirely on the output of the chemical reaction. Atom economy expresses how much desired mass we theoretically could get out of a chemical reaction versus the total mass of all products. AE is a crude indication of how much waste there might be in our chemical reaction -- how much waste we are *designing* into our reaction from the very beginning. As such, intentionally increasing the (theoretical) atom economy addresses the first Green Chemistry Principle:



I emphasize *theoretically* here because atom economy is based entirely on just knowing the balanced chemical equation (the theoretical stoichiometry) for a chemical reaction, not anything about any actual reaction details, such as amount of reactants, limiting reactants, side reactions, etc. Early on in our design for the Green Chemistry Assistant, we decided that the site should help students understand what atom economy is about, but that should not be the focus. That is, the site should not itself be a virtual workbook for learning how to calculate atom economy. (That would be a different tool.) So when a student enters a balanced equation, the atom economy is instantly calculated (Figure 1).

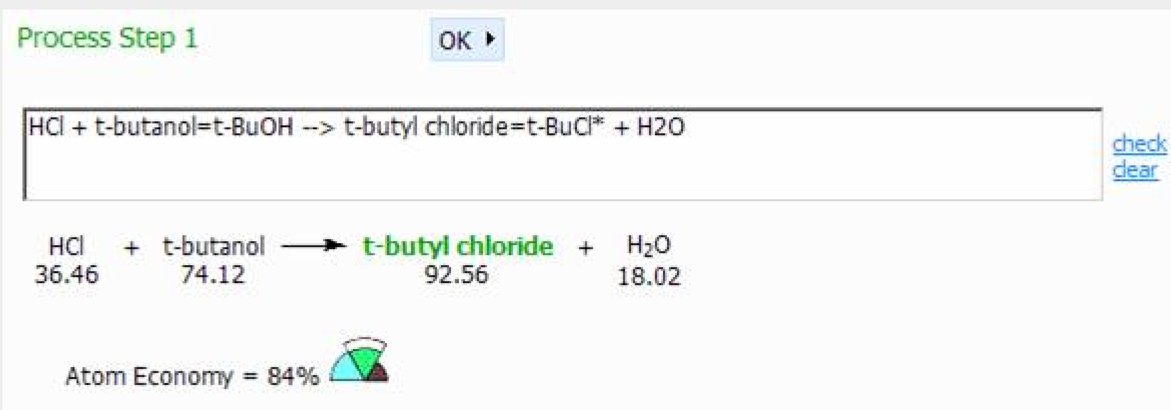


Figure 1. When a valid equation is entered, atom economy is calculated immediately.

Note that the report produced by the GCA does detail the method of calculation (Figure 2) for atom economy.

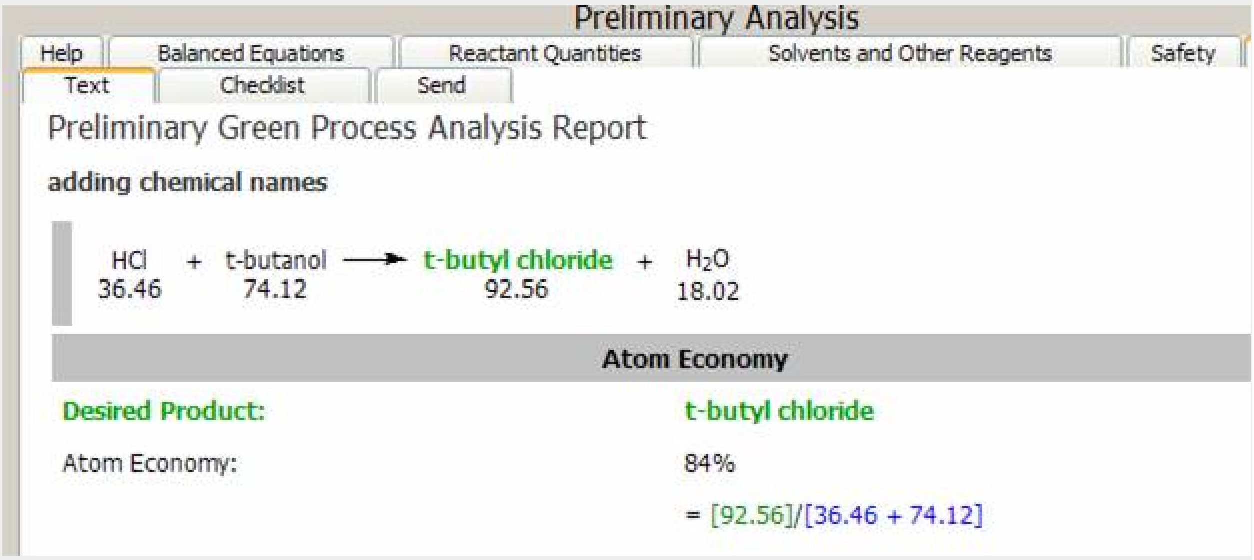


Figure 2. The final report page details how the atom economy was calculated.

We debated at length whether it was wise to "tell all" in this regard. Shouldn't students be required to demonstrate that they know how to calculate the atom economy themselves? The answer we arrived at was this: Absolutely. Just not here. We can save that for the exam. We'll get back to this issue below, in the section on what we've learned about our students.

What the Green Chemistry Assistant emphasizes is that atom economy is just one simple example of the much richer variety of green chemistry measures that can be discussed in relation to a chemical process. After all, the balanced chemical equation is only a beginning.

Balanced Chemical Equations and *Intentionality*

In organizing the information flow of the Green Chemistry Assistant, we realized that there really are three separate contexts that chemists need to consider when going into the laboratory. The first is the writing of a *balanced chemical equation*. Now, obviously, one can do a chemical reaction and not have a clue what the balanced chemical equation for it is (students in my labs do this all the time!), but at least in the introductory chemistry arena, we tend to emphasize that balanced chemical equations are important. They tell us what the reactants and products are, and how they are related in terms of moles - the *stoichiometry*.

When we applied the Green Chemistry Assistant to first-year chemistry, we quickly realized that thinking about chemical reactions in terms of green chemistry introduces a whole new concept to the first-year curriculum:*intentionality.* Thus, while it may be straightforward to balance any given chemical equation, one cannot proceed even to the simple concept of atom economy without discussing *why* a chemical reaction is being performed - Is this reaction one that produces water in a special way, or is it the t-butyl chloride that we are after? What is the chemist's*intent*? Is one of these products going to have to be considered waste? The key word here is "desired" as in *desired product*, and the complementary term generally unknown (at least at St. Olaf) in the entire undergraduate curriculum is the idea of a *coproduct* - a stoichiometric product of the reaction, present in the balanced chemical equation, but not one that we particularly desire. Green chemistry provides much more than just a new way to see if students can use their calculator; it gets them thinking about why anyone would want to do chemistry in the first place. An atom economy of 80% tells us that only 80% of the mass we put into a chemical reaction is going to come out as something we actually want. The rest will probably be waste.

The Experimental Reaction

Beyond the balanced chemical equation, we can consider the reaction itself - how much of each reactant is involved, what the limiting reactant is, what catalysts might be involved. More green chemistry measures arise (Figure 3), because there is more opportunity for *intentional waste*. Now we have the ideas of a limiting reactant, a theoretical yield, and the less familiar *relative excess* and *experimental atom economy*.

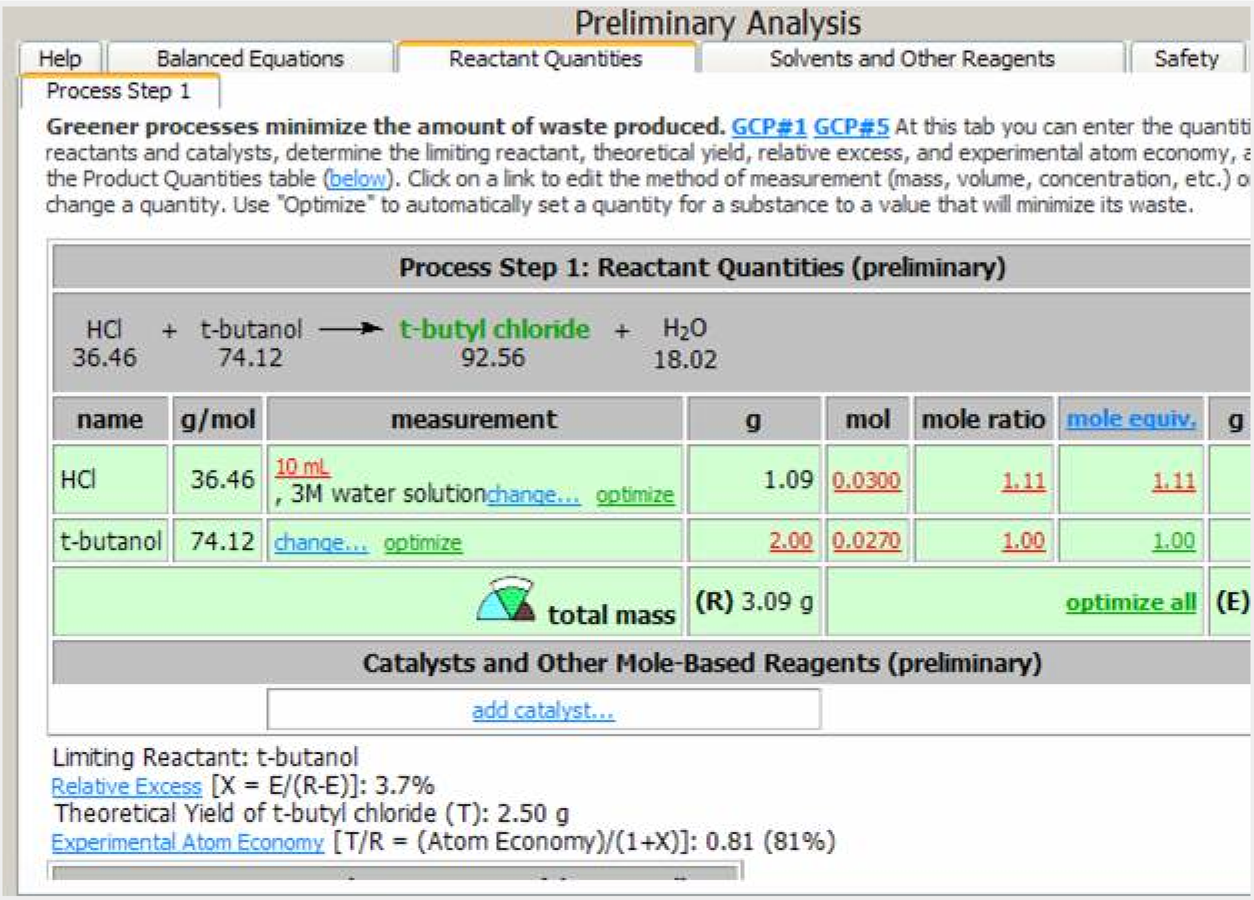


Figure 3. Reaction considerations include the exact amounts of reactants used, how much of each is left over after the reaction, and what other sorts of mole-based reagents and catalysts are employed.

Relative excess (X) is simply a measure that relates how much excess mass we are using (E) to how much we *hope*will be utilized in the reaction (R - E), where R is the total amount of reactants employed.

$$\textbf{Relative Excess} = \frac{\textbf{(excess mass)}}{\textbf{(utilized mass)}}$$

A relative excess of 0% is good - we are putting in just the amounts that can react. There is effectively no limiting reactant, and there should not be any reactant left over at the end. A relative excess of 100% (or more!) is dismal - it means that even from the very first moment of the reaction design we are *guaranteeing* that we will have at least as much waste to deal with as desired product.

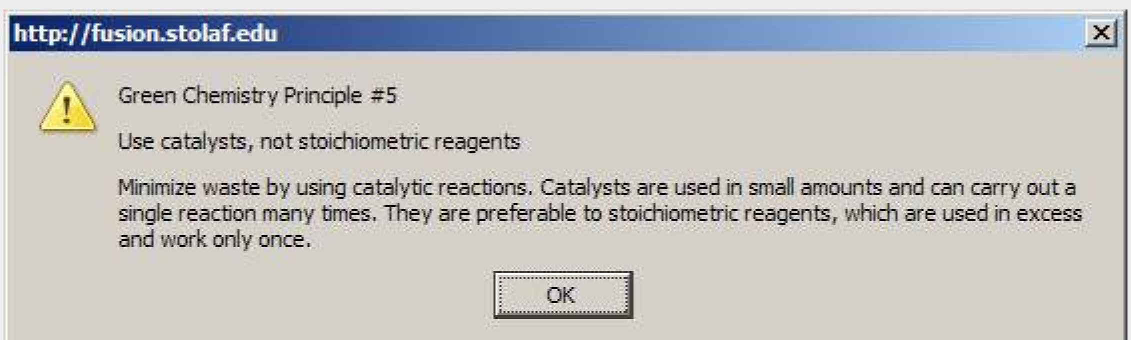
Experimental atom economy is simply a measure that relates theoretical yield of desired product (T) to the actual amounts of reactants being used (R) rather than to the theoretical amounts based just on the balanced chemical equation. It is related to "theoretical" atom economy by the relative excess:

$$\textbf{Experimental Atom Economy} = \frac{\textbf{(Atom Economy)}}{\textbf{1 + (Relative Excess)}}$$

Note that since any excess reactant mass is in the denominator here, the experimental atom economy is *at most* the atom economy and more likely will be somewhat lower.

Catalysts and Reaction Optimization

It is at this stage in the green chemistry analysis that we consider catalysts and other mole-based reagents needed for the chemical reaction, although they do not figure into the calculation yet. We do this because the sorts of calculations involved (determining molar masses, calculating molar ratios) are more similar to what is done for reactants than what will be done for solvents.



In addition, it is at the reaction consideration stage that we might start to think about how we might optimize the reaction. Here the Green Chemistry Assistant can do some pretty fine magic. Want to know how much HCl is "just enough"? Click on "optimize" there and see what happens (Figure 4). Now we have no relative excess, and the experimental atom economy is a bit higher. It looks like we might be able to get away with using only 9 mL of 3 *M*HCl solution instead of 10 mL. (Of course, that brings up other considerations, doesn't it?)

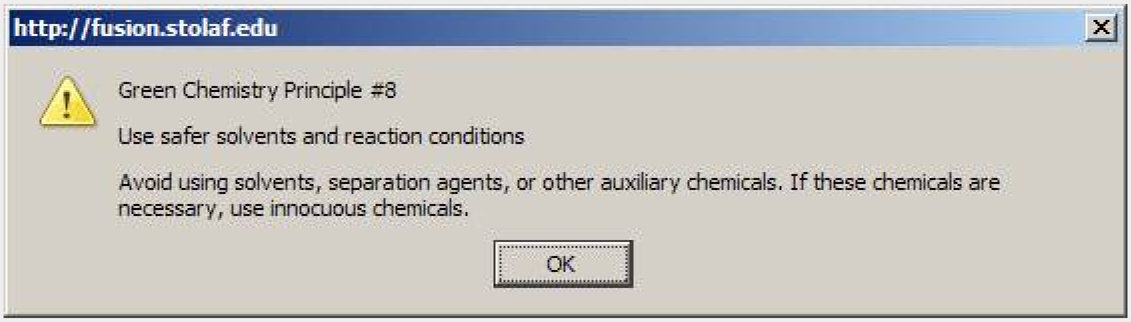
Process Step 1: Reactant Quantities (preliminary)							
HCl + t-butanol → t-butyl chloride + H_2O 36.46 74.12 92.56 18.02							
name	g/mol	measurement	g	mol	mole ratio	mole equiv.	g excess
HCl	36.46	8.99 mL, 3M water solution change...	0.983	0.0270	1.00	1.00	0
t-butanol	74.12	change...	2.00	0.0270	1.00	1.00	0
total mass			(R) 2.98 g	optimized			(E) 0 g
Catalysts and Other Mole-Based Reagents (preliminary)							
		add catalyst...					

Limiting Reactant: HCl
Relative Excess [X = E/(R-E)]: 0.0%
Theoretical Yield of t-butyl chloride (T): 2.50 g
Experimental Atom Economy [T/R = (Atom Economy)/(1+X)]: 0.84 (84%)

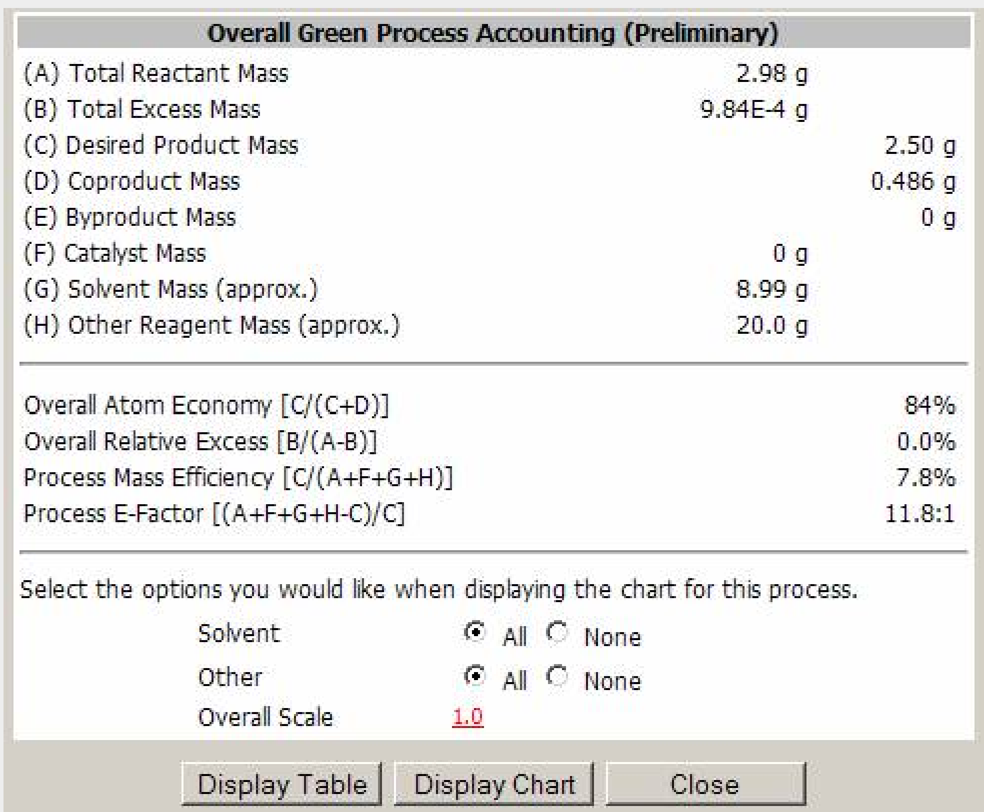
Figure 4. Reaction considerations after optimizing, showing that, in principle, we didn't need so much HCl.

The Chemical Process

Our conceptualization of what goes on in the chemical laboratory continues now to one more stage: the chemical*process*. Beyond the balanced chemical equation, beyond considerations of actual amounts of reactants, we must consider reaction conditions. How much energy is this going to take? What solvents are we going to use? What materials will we have to employ in order to isolate and purify the desired product? What hazards are involved? This brings us to another Green Chemistry Principle:



These are the *nonstoichiometric* aspects of the chemical reaction that often play a major role in a full green chemistry analysis. Now we have measures such as *process mass efficiency* and *process E-factor* and something we are calling the "Overall Green Process Accounting" (Figure 5).



Overall Green Process Accounting (Preliminary)

(A) Total Reactant Mass	2.98 g	
(B) Total Excess Mass	9.84E-4 g	
(C) Desired Product Mass		2.50 g
(D) Coproduct Mass		0.486 g
(E) Byproduct Mass		0 g
(F) Catalyst Mass	0 g	
(G) Solvent Mass (approx.)	8.99 g	
(H) Other Reagent Mass (approx.)	20.0 g	
Overall Atom Economy [C/(C+D)]		84%
Overall Relative Excess [B/(A-B)]		0.0%
Process Mass Efficiency [C/(A+F+G+H)]		7.8%
Process E-Factor [(A+F+G+H-C)/C]		11.8:1

Figure 5. A summary accounting of the masses of reactants and products for our process, including two new measures: process mass efficiency and process E-factor.

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Process Mass Efficiency (PME) is basically an extension of the reaction mass efficiency idea. Here it means the theoretical mass of desired product divided by the total mass inputs for the reaction, including catalysts, solvents, and any other potentially nonrecyclable material. It's a sobering number - just 7.8% in this case, and suggests all sorts of ideas for possible improvements, from using less solvent to being more efficient in our product isolation.

$$\textbf{Process Mass Efficiency} = \frac{\textbf{(Theoretical Yield)}}{\textbf{(total input mass)}}$$

Process E-Factor expresses the ratio of total mass expected to be lost over the theoretical yield of the desired product. It turns out also to be (1/PME - 1). "E" here stands for "environmental." It's telling us the ratio of waste tononwaste. A process E-factor of 10 means that we expect to generate 10 times as much waste by mass than we plan to get out of the reaction in the form of desired material.

$$\textbf{Process E-Factor} = \frac{\textbf{(total waste mass)}}{\textbf{(Theoretical Yield)}}$$

These, then, are the calculations that the Green Chemistry Assistant delivers as a *starting point* for talking about the relationships among reactants, desired products, and coproducts; the ways in which a reaction might be optimized, and the overall efficiency of a proposed chemical process. This is really all the Green Chemistry Assistant does.

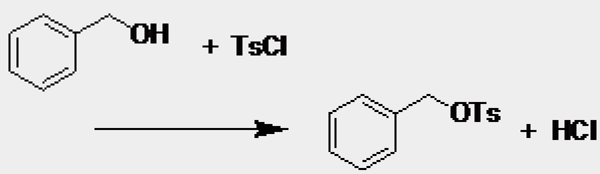
Preliminary vs. Final Calculations

Note that everything mentioned up to this point involves just *preliminary* considerations. These discussions have been incorporated into our prelab assignments in our organic lab. Within the next year we hope to add a second component to the Green Chemistry Assistant, one that focuses on the actual yield, the amounts of material actually used in the chemical reaction, and the extent to which any material might have been recovered or recycled.

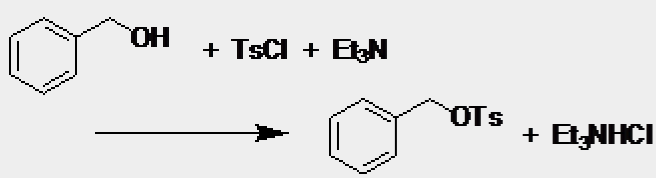
How has having had easy access to these calculations changed our pedagogy?

What has been interesting for me personally is how *our own* access to the GCA has changed the way we teach organic chemistry. The first hard lesson we learned, working only with advanced research assistants, was that it was far more difficult *just to get the balanced chemical equations* than we had ever imagined. I was actually quite stunned to realize just how difficult it was (even for me) to write the balanced chemical equation for an organic experiment. Take, for example, the "classic" case for discussion of green chemistry, the tosylation of benzyl alcohol:

OK, here's the question, simple enough: What's the atom economy? I'll bet anything that readers of this paper will not agree on a single number. Why would that be? Because we won't agree on the balanced chemical equation for this reaction. Is it the following, with an atom economy of 88%?



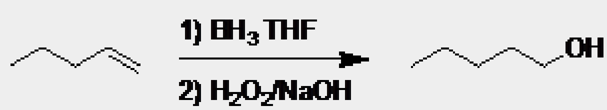
Or should we include triethylamine in the balanced equation and claim that the atom economy is only 66%?



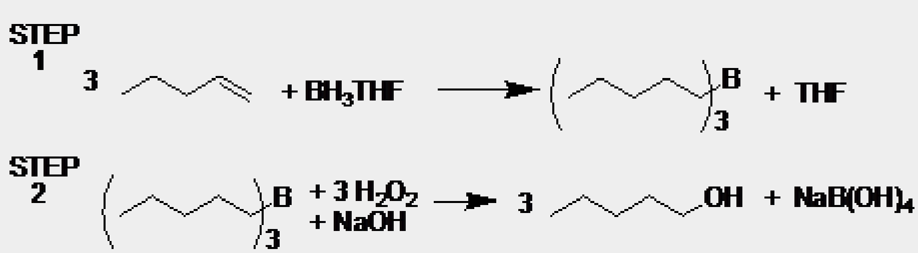
I suggest that inclusion of triethylamine is reasonable and defensible. Yet the original account describing atom economy chooses the first of these analyses. Who is right? Perhaps our thinking along these lines needs to evolve. Perhaps what we are seeing here is the difference between thinking in terms of just a single reaction (early green chemistry) and thinking in terms of an overall process. From a reaction point of view, maybe we can ignore thetriethylamine; but from a process point of view, how can we ignore the fact that our coproduct HCl takes with it a whole mole of triethylamine for every mole of benzyl tosylate produced?

The Complication of Multiple Process Steps

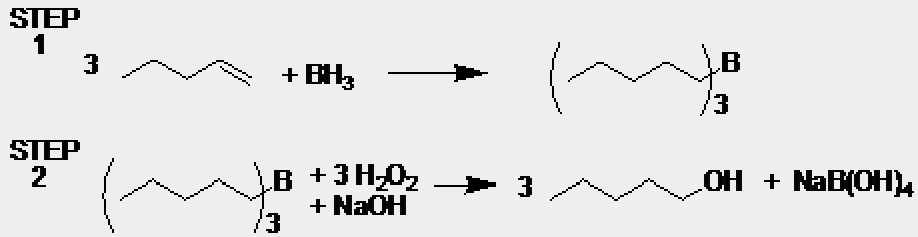
Right off the bat, when we started to work with actual experiments students were doing in lab, we realized that the typical processes carried out in the organic lab by students involve more than one reaction, with more than one balanced chemical equation. In trying to conceptualize an actual lab experiment in terms of equation, reaction, and process, we realized that we needed to be much more explicit. We needed process *steps.* Another example:hydroboration/oxidation of an alkene to produce an alcohol.



Now here is an example that gets us deep into process thinking. Obviously we have two steps. We can't just write one single balanced chemical equation. Perhaps we write:



The overall atom economy calculated for this set of equations is 60%. But was it really appropriate to include thetetrahydrofuran (THF) as part of the reactants? Isn't it really just solvent? Might not a perfectly capable practicing chemist have written instead the following?

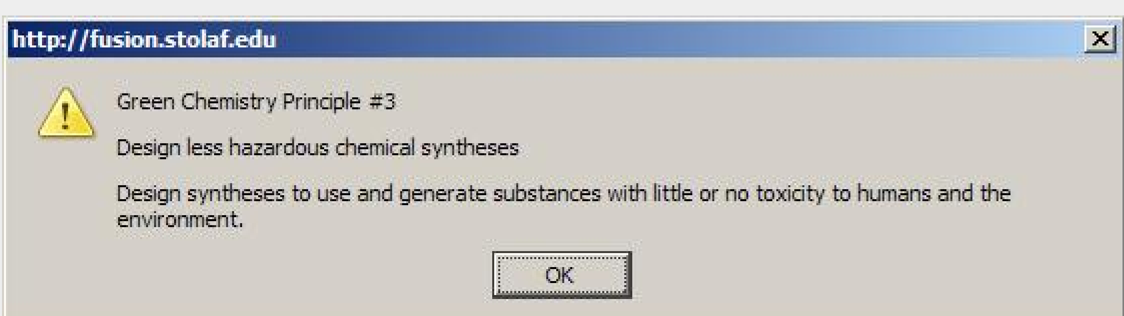


Now the overall atom economy is 72%. But that's not all. We obviously have the *coproduct* $NaB(OH)_4$. But we would be well advised to discuss with our students the additional possibility of a *byproduct* - in this case, hydrogen gas, H_2, produced at the end of the reaction when water is added in the presence of excess borane. So maybe there are three steps here...

These are not isolated examples. My point is not to emphasize how difficult this is. My point is simply that the path to green chemistry measures has all sorts of interesting twists and turns and allows quite a variety of discussions related to important laboratory considerations. Doing this analysis *ourselves*, as instructors, may be at least as beneficial as having students do the analysis. We have rewritten many of our labs in an attempt to help students see more clearly the *process* that they will carry out in lab -- what the actual steps are going to be, whatcoproducts and byproducts are to be expected, and - most significantly - what hazards are involved.

What is the connection to laboratory safety and waste management?

Which brings us to my final topics, laboratory safety and waste management, and another Green Chemistry Principle:



Bringing to students a responsible awareness of chemical safety and waste management issues has probably been *the*most valuable aspect of bringing green chemistry into the undergraduate curriculum. This, then, is our connection to the United States Environmental Protection Agency. The Green Chemistry Assistant can tap into an EPA database of over 60,000 compounds, providing access to registry numbers, as well as toxicity and general chemical hazard information (Figure 6).

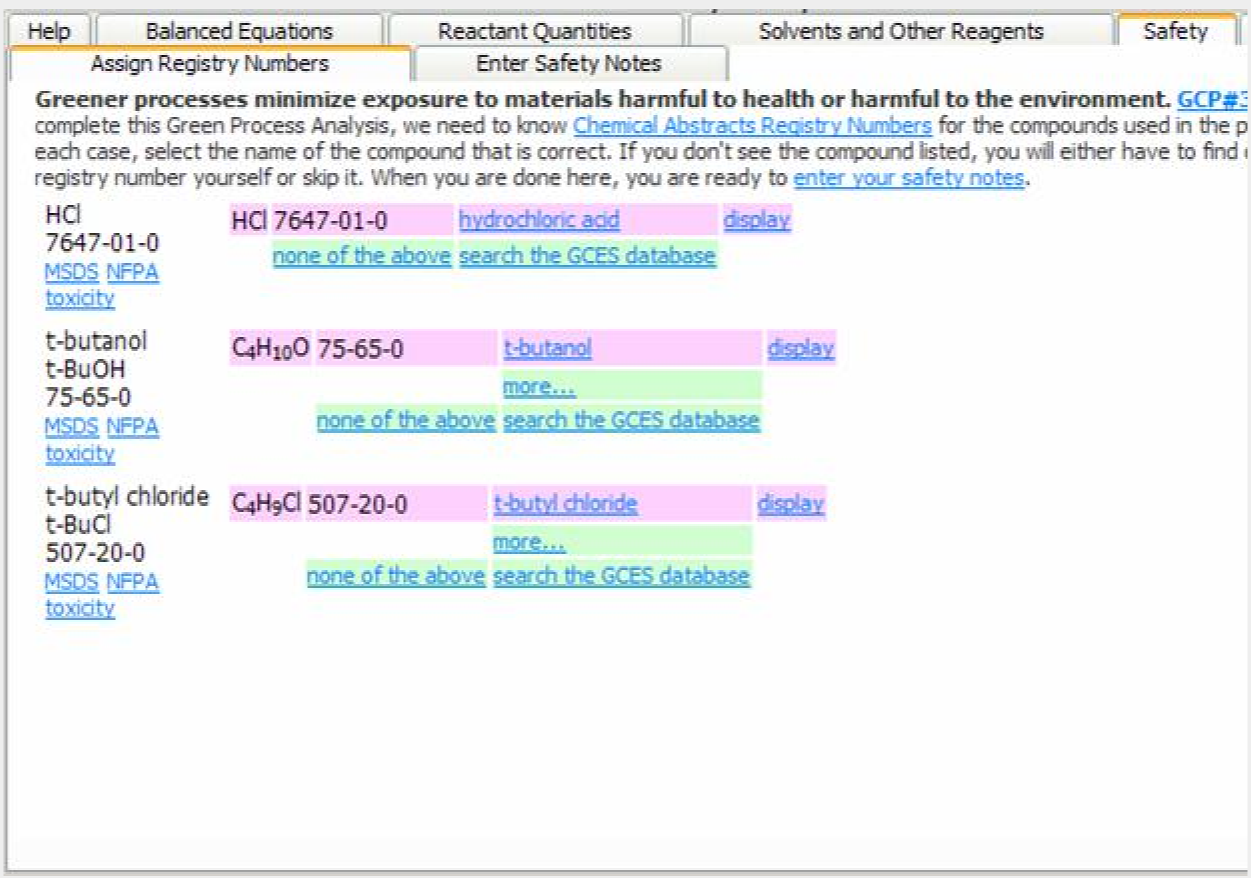
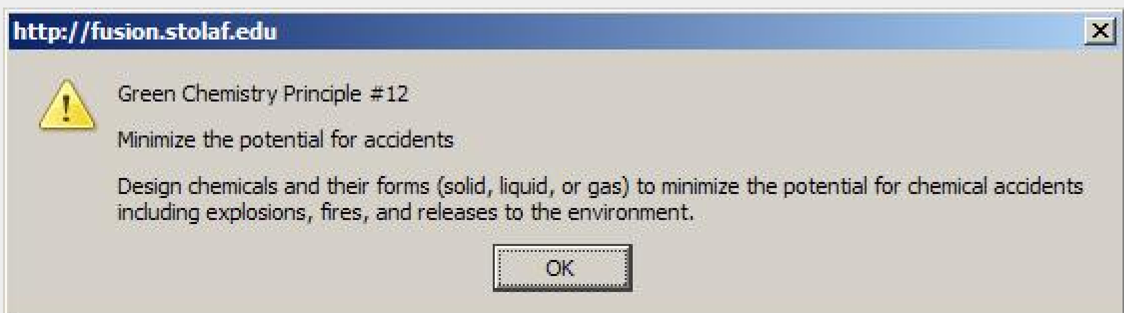


Figure 6. Matching a reactant or product to a registry number can be a useful the first step in accessing the chemical safety information for that compound. The GCA taps into an EPA database containing over 60,000 common chemicals.

To a large extent, getting students *and faculty* thinking responsibly about chemical hazards is what green chemistry is all about. Students need to take responsibility for their work in the lab in exactly the same way as workers in industry need to take responsibility for their own environment. Helping students see the extent to which practicing chemists consider these issues (and still go about their business) is a major first step. The whole concept of a "chemical registry" and the tie in to nomenclature, for example, can be highly instructive.

Overall Process Design

Green Chemistry focuses on the process design. The whole point here is that laboratory safety and waste management are both *design* issues.



I'll finish up with one creative use of the Green Chemistry Assistant that could potentially help any laboratory manager. This is the Assistant's capability to produce "scaled up" reports (which are E-mailed to the user for safekeeping). If one generates a report for some lab process that the students are doing and then scales it up by the number of students in organic chemistry, one can quickly see the expected material and waste issues (Figures 7 and 8).

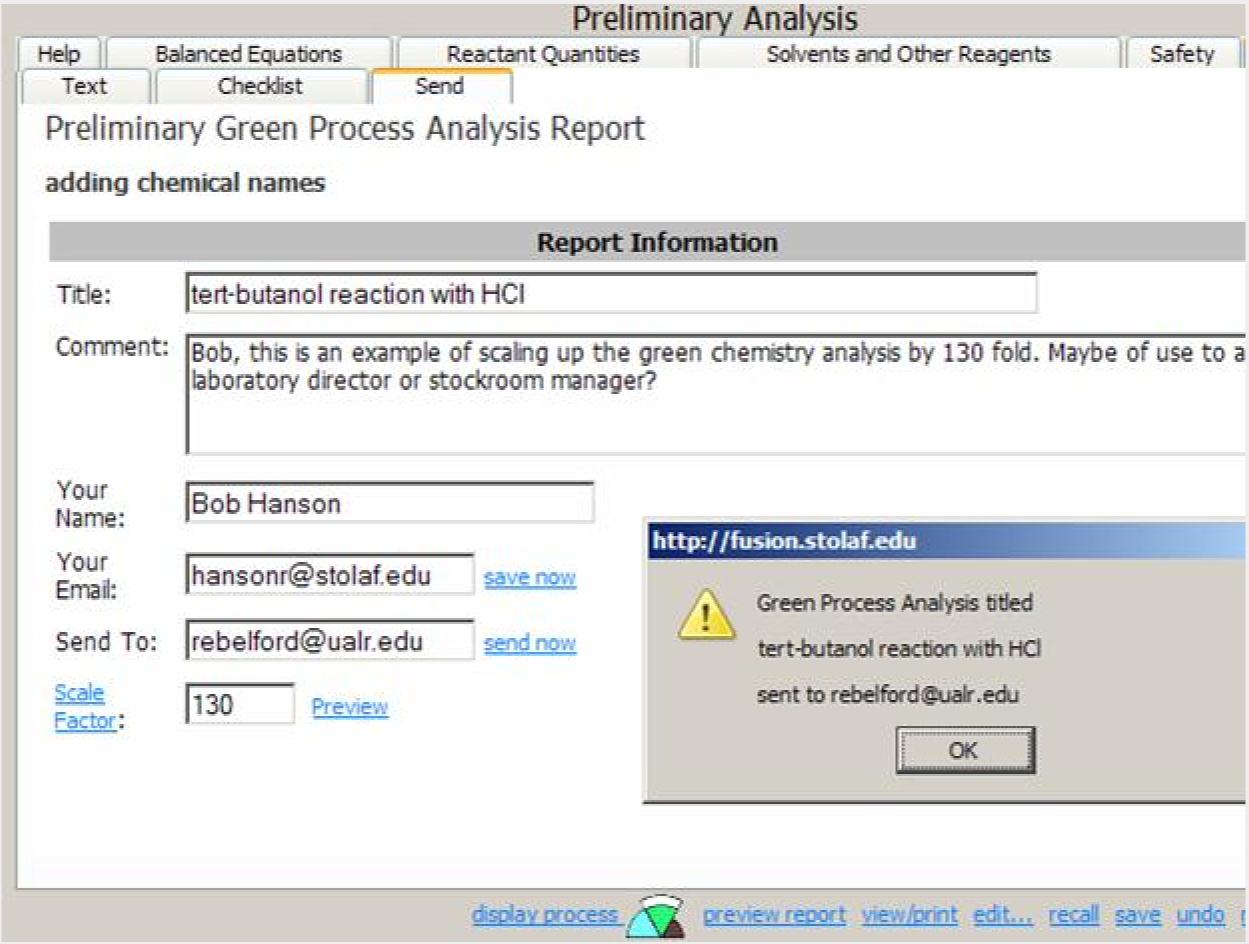


Figure 7. Scaling up a report and sending it to a colleague or oneself.

Desired Product:	**t-butyl chloride**
Theoretical Yield:	324.52 g

Percent Excess					step atom economy	
Step	**g input**	**g used**	**g excess**	**% excess**	**equation**	**experimental**
1	387.4	387.4	0	0.0%	84%	84%

Step 1 Reactant Quantity Details				
name	**formula**	**mol**	**g/mol**	**g**
	HCl	3.51	36.46	128
Safety Notes: no safety notes for this compound		1168.7 mL, 3M water solution		
t-butanol	t-BuOH	3.51	74.12	260
Safety Notes: no safety notes for this compound				

Preliminary Product Quantities				
name	**formula**	**mol**	**g/mol**	**g**
t-butyl chloride	t-BuCl	3.51	92.56	325
Safety Notes: no safety notes for this compound				
	H_2O	3.51	18.02	63.2
Safety Notes: no safety notes for this compound				

Figure 8. Part of the final report, scaled up 130 times and showing how much of each reactant will be needed as well as how much of each product (aka "waste" in an undergraduate lab) is expected to be generated .

Summary

Using the Green Chemistry Assistant, students as well as instructors and laboratory managers can do common calculations in relation to green chemistry quickly and efficiently. Though just another tool, the GCA is certainly much more. It is a true *web application* that has allowed us to dig far deeper into the concepts of green chemistry and to see much more clearly the interrelated steps in an overall chemical *process* than we have been able to do previously. The Green Chemistry Assistant is really no more than a tool, a glorified calculator. Nonetheless, its value goes far beyond showing students how to calculate atom economy. By its very organization, the GCA provides a basis for talking about chemical processes at the balanced chemical equation, experimental reaction, and overall process levels, suggesting means for reaction and process optimization, and even opening up the opportunity for experimentation in the area of green chemistry. By providing links to chemical safety-related databases, including MSDS, NFPA, and toxicity information, students as well as instructors are empowered to design better, more efficient, less toxic, less wasteful chemical processes for use in the undergraduate chemistry laboratory.

Acknowledgments

I am indebted to all the many undergraduates who have put up with us during the early development phase of the Green Chemistry Assistant. I particularly wish to thank Paul Campbell, St. Olaf '06, who worked diligently to test and retest and further test the interface during the summer of 2005. The idea behind the Green Chemistry Assistant started with an effort to develop the Green Chemistry Expert System (GCES) into more student-friendly form. Mank thanks go to Rich Engler, US EPA, who has been intrumental in working with us in that regard. Dan Beach, St. Olaf IT staff, was very helpful in our setting up the ColdFusion side of the operation. In addition, many thanks are due to Irv Levy, Julie Haack, Gary Spessard, and Marc Klingshirn for their helpful discussions and unwavering commitment to green chemistry. This work was supported by a *very* generous grant by the W. M. Keck Foundation.