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Upon Further Review: A Commodity Chemist on Green Chemistry

Abstract:
Green chemistry is most often thought of in the context of specialty or pharmaceutical chemicals where many synthetic chemistry approaches are in play. However, principles similar to those of green chemistry and engineering were employed over the years in reducing cost and increasing volume of chemicals that became commodities. This paper considers some of those principles, their impact, and some perspectives on the potential and limits associated with green chemistry for commodity chemicals.

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During the year I was president of the American Chemical Society (ACS), 2005, I was the head of our delegation visiting China. It was a joy to return to see the progress the Chinese people had made since my first trip on behalf of my employer, nearly 20 years before. In addition to the challenge of a week of eating two banquets a day, I had the privilege of meeting literally hundreds of bright and serious students and professors. It was a wonderful time.

One particular exchange stood out. At Tsinghua University in Beijing, we had an interesting and wide-ranging roundtable discussion with students and professors about chemistry and industry. Now, while the situation there may be different in 2015, during that discussion in 2005 one student asserted, "Of course we know that pollution is inevitable with growth and progress."

I was stopped. In a moment, the history of the past 30 years of the chemical industry as I have known it went through my mind. I thought about the advent of voluntary chemical and safety programs like Responsible Care® and OSHA Star, and the difference they made in my company and in the industry. I thought about the progress we have made in our own universities in educating students in the principles of green chemistry. To tell the truth, when I was in that student's place 30 years ago, I might have made the same statement. But 30 years later it seemed unimaginable.

You see, we have changed innumerable things in the practice of chemistry, but the most important thing we have changed is our minds. I couldn't let that student's statement pass.

> I said, "Please forgive me, but I need to disagree." From the perspective of the chemical industry, pollution and progress are not synonymous. Pollution is waste and waste is cost. Progress is benefit and a better quality of life. The two things are inherently different. That understanding is fundamental to what we call Green Chemistry. Your job as a chemist is to solve problems, to be sure. However, it is not to find a solution to a technical problem, but to challenge yourself constantly to find a better solution – that is, more benefit and less cost. I suggest you visit the ACS website and learn about the Green Chemistry Institute (GCI)."

This student, before even entering the working world of chemistry, had resigned himself to defeat. It shows the depth of the misconception, the difficulty of changing minds, and the importance of the principles of green chemistry in remediating this perception problem.

To me, the message of green chemistry and engineering is whether your particular point of emphasis is environmental, as in minimizing pollution, or economic, as in minimizing cost, the principles are important tools for accomplishing your goal. And frankly, I've found that once made aware of them, my fellow chemists and engineers working in industry find most of them nearly intuitive.

What I've just described to you are the technological underpinnings of green chemistry as I see them. We in ACS have always viewed it as a process of innovation, driven by scientists in discovery mode. We have been clear: green chemistry is not a regulatory program, because regulation tends to narrow the field of thought and not expand it. On a previous incarnation of the front page of the Green Chemistry Institute (GCI) website, it said:

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> Green Chemistry differs from previous approaches to many environmental issues. Rather than using regulatory restrictions, it unleashes the creativity and innovation of our scientists and engineers in designing and discovering the next generation of chemicals and materials so that they provide increased performance and increased value while meeting all goals to protect and enhance human health and the environment [1].

As I write this, it is 10 years later. I am in my last week of a 36-year career with a commodity chemical manufacturer. Over that time I've learned that "The Chemical Industry" is not one thing: commodities are different from specialties, which are different from fine chemicals or pharmaceuticals. Each segment views its business differently because the costs and prices and products and customers are different.

I'd like to expand a bit about two of these segments, commodities, and specialties. Commodity chemicals are manufactured in large volumes. Typically, most of the cost associated with a commodity is raw material cost or the capital cost of the plant. Relatively less of the cost of a commodity is tied up in labor, advertising, or R&D.

The main thing that distinguishes a commodity from a specialty is that commodities are fungible; that means that one company's version is indistinguishable from another company's version. Commodities are difficult if not impossible to brand or differentiate. These things are directly the opposite of specialties, which can be custom-made, distinguished by manufacturer, branded, and sold at a premium price because of the differentiation.

So why would someone whose career was spent in the commodity chemicals industry be writing a paper about green chemistry? Perhaps I have a different and counterintuitive perspective on the benefits of green chemistry. In this paper I'd like to make three points.

First, many commodities – certain chemicals produced at low relative cost and high volumes – got that way because of chemistry and engineering operating principles that are indistinguishable from at least some of the principles of green chemistry and engineering. These principles were used to take cost out of chemical manufacturing.

The second is similar. Done correctly, the benefit of green chemistry, particularly in commodity markets, may be as much economic as it is environmental, although both are likely to occur simultaneously.

Finally, green chemistry's greatest potential impact is on energy.

Anyone who has spent time with the principles of green chemistry and green engineering knows it is difficult if not impossible to optimize all of them simultaneously in the preparation of a chemical or product. In manipulating conditions, there is a need to simultaneously consider a number of response variables – from energy use, to greenhouse gas generation, to chemical hazard or even cost – even as the principles provide guidance on how to proceed. The principles do not always point in the same direction for all responses, which become a dilemma for those who are engaged in what is known as alternatives assessment: devising means to eliminate chemicals of concern while minimizing process impact and providing efficacy at a cost the market can afford.

I've always viewed the principles of green chemistry and green engineering as checkpoints in chemical and process design. For me, the principles read: "All things being equal, consider this before considering that." Not absolute rules, but points to be taken on board. And when they send you different directions, choices must be made.

Here are some thoughts on the relationship of commodity chemicals to green chemistry.

1 Commodity Chemicals Got That Way Through the Use of Principles Identical to Many of Those of Green Chemistry and Engineering

Perhaps the most commodity of all the commodity chemicals is ethylene. Hundreds of billions of pounds of it are made globally every year. It is the basis of most of the commodity polymers. It is also a natural product that enhances fruit ripening. And for all the volume we produce today, when the polymer industry was new, ethylene was a challenging material to make.

In the 1920s, ethylene was made by dehydrating ethanol, which was obtained from fermentation. Prior to the development of the polymer industry, most of that ethylene was reacted with bromine to make ethylene dibromide, an additive in leaded gasoline. For other industrial processes, when a two-carbon unit was needed, it could be obtained by functionalizing acetylene, which was made by adding water to calcium carbide.

As automobiles became more popular, engineers at Dow Chemical Company started working on a process to make ethylene from naphtha, a petroleum distillate [2]. Availability of ethylene increased with the more robust process and a more abundant raw material for its synthesis. Today, in many countries, naphtha is the raw material of choice for ethylene. Most of the ethylene in the United States is made by dehydrogenating ethane, harvested from natural gas.

Consider some green chemistry implications of these three processes. Calcium carbide is made from coke and limestone, heated in an electric arc furnace at 2,000°. The ovens are highly energy intensive, and the process itself (as well as coke production leading to it) can be extremely dirty. After making acetylene, two to three times the mass of acetylene is left behind as calcium hydroxide waste. Ultimately, this material can be dehydrated to make lime and used in making cement if the volume and location matches, but it is yet another process.

Dehydrating ethanol is somewhat less daunting, but was limited by the capacity to produce it, particularly in the 1930s. Then, dehydration was catalyzed by sulfuric acid. Today, it can be accomplished thermally at ca 250 °C over a zeolite catalyst. By the nature of a dehydration reaction, 100 % molecular conversion is only 61 % mass conversion.

The steam-cracking process utilizes a hydrocarbon raw material, generally ethane or other liquefiable hydrocarbons separated from natural gas. Steam is both a heating source and a diluent; the process takes place at about 850 °C, quickly, and with a fast quench, maintaining appropriate dilution and kinetic control. Steam cracking of ethane yields ethylene and hydrogen from nearly 80 % of the starting material. Minor side products include methane, propylene, butadiene, and other C_4s, all useful hydrocarbons. There is virtually no waste [3].

The steam-cracking process is the dominant process in the world. It became so because of the difficulty, resource use and high cost associated with the other processes. For local reasons, calcium carbide for acetylene production is done industrially only in China; producing ethylene from ethanol is done for marketing purposes to make plastics from biologically based materials.[1]

From the first indication that steam cracking could produce ethylene, engineering principles congruent with many of the principles of green chemistry came into play, and at maturity this process scores fairly well on a lot of them. Nearly perfect score on preventing waste, atom economy, and avoidance of solvents and derivatization, particularly compared to the carbide process. Neither ethane nor ethylene itself is highly toxic, and the steam-cracking process uses little if any toxic ingredients.

On the other side of the coin, some of the principles are challenging. Since the target is a two-carbon hydrocarbon, there's not much that can be done to reduce the inherent flammability or explosivity of the material. The process is done at high temperature and pressure and carries an energy cost; it is difficult to imagine the reaction occurring at ambient conditions.

Designing for degradation is a function of the downstream products, so all three processes fare the same. While the carbide process is clearly inferior on environmental (and cost) grounds, life cycle assessment is appropriate to score the other two, comparing ethanol production and taking into account atom economy of the two processes. If, however, production cost could be used as a crude surrogate for resource use, the ethane steam-cracking process is less costly.

Perhaps the principle of green chemistry that is most daunting for commodities is the preference for renewable resources, which in this case I take to mean bio-based raw materials. I see three challenges in this regard, which I will abbreviate as scale, substitution, and life cycle considerations.

1.1 Scale

In 2014, about 14 billion gallons (92 billion pounds) of ethanol was produced in the United States, mostly from corn. At 100 % yield that would produce about 60 billion pounds of ethylene, similar to the US production. If all US ethylene were to be made from ethanol, even though the raw material supply is evenly matched, the dehydration plants to accomplish this would have to be built, and because of the physical properties of ethylene they would need to be built with pipeline access to downstream users, and ethanol would have to be transported to them.

But the biggest question: all of that agricultural production would go to manufacture just one commodity chemical. The United States manufactures about 25 % of the world's ethylene, and whether there could be bio-based raw material in the other countries of the world is unknown.

1.2 Substitution

The National Academies report "Sustainability for the Nation: Resource Connection and Governance Linkages" [4] discussed the magnitude of the US government program, subsidizing ethanol production and the impact it had on the marketplace. The policy subsidizing fuel use of ethanol had the unintended consequence of pushing Midwestern farmers out of soybeans and into corn. Soybeans became short and induced farmers – largely in Brazil – to plant soybeans to replace lost volume:

> Connections that are indirect can nonetheless be highly significant. Demand for ethanol in the United States caused the price of corn to rise and caused a shift in land use from soybean production to corn production. To fill the void, land was deforested in other countries and planted in soybeans.

Accepting that corn is a poor agricultural feedstock for ethanol, similar substitution consideration would have to be carried out regarding the advisability of ethanol-to-ethylene even if derived from higher sugar-yielding crops. The Dow-Mitsui plant was designed for 720,000 m^3 ethanol /114,000 ha sugarcane (ca 2 tonne/acre). The US ethylene capacity is about 25 million tonnes and would at best require significant redeployment of land – on the order of thousands of square miles – to sugarcane, or a switch of ethanol use from fuel to chemicals, presumably replaced by fossil products.

Early in this century, a similar dynamic drove the palm oil market – approximately the same size globally as US production of ethanol – into unsustainable land use, particularly with respect to indigenous animals and the risk of an agricultural monoculture. The situation has improved with acceptance of principles developed by the Roundtable on Sustainable Palm Oil [5]. It is difficult to know what impact another program of similar size would have on agriculture, particularly if farmland currently producing food were taken out of service in favor of a crop designed to produce raw materials for commodity chemicals globally.

1.3 Life Cycle Considerations

In order for a chemical raw material to be truly sustainable, it should be a material that is sustainably grown specifically for this purpose or is derived from a material not currently being used productively. Producing ethylene from corn stover cellulose, which appears to be a waste, seems like a good idea, but those corn stovers are currently plowed under for soil amendment. Starting from a crop that is purpose grown – switchgrass or another "fallow field" product – or repurposing of truly waste cellulose headed for landfill (and not paper recycling) might pass the life cycle test at some scale. Whether it could do so at tens of billions of pounds is an open question.

Two of the winning entries of the 2015 Green Chemistry Challenge awards involved the use of industrial off-gases or CO_2 as feedstock. The first innovation routed off-gases from steel mills to genetically modified organisms capable of converting them to ethanol, acetic acid or 2,3-butanediol. The second involved a new photobioreactor for fixing CO_2 via blue-green algae. Either would fit the requirement of turning not just a waste but a pollutant into necessary products.

However, 37 years of experience asks whether such processes will scale to the kinds of volumes we're talking about, and if so, will they be cost competitive, both fixed and variable? It would be wonderful if the answer were yes on both counts. But for now, bio-based solutions for the chemical industry will work best where the amounts are manageable, genetic modification in a factory environment is tolerated (1,3-propanediol converted by bacteria from glycerol, for example) or where the chemistry takes advantage of a unique molecular scaffold produced biologically.

2 The Benefit of Green Chemistry May Be as Much Economic as It Is Environmental, Although Both Are Important

In the book *Eco-Efficiency*, Frank Popoff and Livio DeSimone, two former chemical industry CEOs, described the perhaps counterintuitive notion to some that when you reduce pollution you often times also reduce costs – although sometimes they are hidden costs that are not always fully recognized by our accounting system [6]. And, conversely, a responsible process of cost reduction generally results in greater efficiency and almost inevitably means a reduction in waste or pollution at some point in the life cycle.

The key is in optimizing those two variables simultaneously. It is, of course, possible to design more environmentally sound processes that are so costly that they will never be commercialized. Similarly, it is possible to design processes that are "lower cost" but so ignore safety and environmental practices that they are actually not "economical." Just as I advised the Chinese student, more creativity is needed so as to not just find something that works, but to find better solutions on all counts.

John Warner puts it this way: "Green Chemistry really provides a 'holy grail' of sorts: better performance, better cost and 'Oh by the way . . . it is better for human health and the environment.' Given these criteria, what market barrier exists for adopting a greener product save its invention in the first place?" [7].

The GCI, which is a part of ACS, operates a number of industry roundtables, where companies in a particular market space can gather and discuss greener chemistry in a pre-competitive environment. The most successful of these so far is the Pharmaceutical Roundtable [8]. Much of the discussion in the roundtables includes process characteristics: as an example, distillation as a means of separation is ubiquitous. Could less energy-intensive processes be developed? In addition, the roundtables seek simpler synthetic methods that utilize less toxic materials, less organic solvent or fewer waste-generating steps. In either case, while there may well be environmental benefit from reduction of waste generation and disposal, reduced raw material and waste disposal costs are at least a bonus. Other roundtables or other companies that find a similar economic benefit to the use of green chemistry will also be successful, particularly those in cost-sensitive industries.

3 Green Chemistry Can Have Its Biggest Impact if It Enables Green Energy

I've just described an appeal of green chemistry: its perceived potential to reduce resource use and waste. But it is important to put the magnitude of such potential in perspective. The use of coal, oil, and natural gas for fuel is a factor of 10–20 higher than their use for both raw materials and energy in the chemical industry. Even if green chemistry were able to increase the efficiency of the entire chemical industry by 10 % – a huge goal – the overall magnitude of its impact would be less than 1 % on total resource use.

On the other hand, studies of energy efficiency show that only about 45 % of the fuel burned for energy actually gets put to use [9]. The remainder – particularly from the thermal processes that generate electricity – goes to waste heat. One percent decrease in total resource use via green chemistry would be important, but not a game changer.

Some will take this as a cynical statement by a grizzled old denier. Nothing could be further from the truth. The point is: Green chemistry can make wonderful contributions to a company's bottom line by reducing waste, particularly hazardous waste, and by simplifying synthesis, which translates to eco-efficiency. Green chemistry thinking can mitigate potential accidents locally by designing safe processes, choosing materials with a better hazard profile, and mitigating environmental harm, particularly from irresponsible waste treatment. But if green chemistry is truly to make a difference to society writ large it will be because of the contribution it makes to energy efficiency and ultimately use.

Consider the barriers to greater adoption of renewable energy, particularly wind and photovoltaic solar. In both cases, potential uptime has to be taken into account in ways that do not need to be considered for conventional energy. The wind doesn't blow all the time, nor does the sun shine; thus, wind and solar facilities need to be sized at a capacity that is a multiple of conventional plants, and conventional energy generation must be in place to "back up" renewable facilities. On the other hand, contributions made by chemists in the field of energy storage and collection efficiency can allow resizing of such facilities to generate more during peak productive hours with reliable storage and retrieval during nonproductive hours.

Chemistry also could also contribute in harvesting waste heat. In these days, when chemical companies build electrical capacity for their plants they almost always build a combined heat and power facility that is capable of using low-pressure steam or hot water for local heating needs. These plants reach 60–70 % efficiency rather than 30–40 %. Thermoelectric materials if developed could be retrofitted into existing plants to harvest heat from low-pressure steam or hot water. And the real holy grail for chemistry is storing nontraditional energy by splitting water into hydrogen and oxygen, and mimicking natural photosynthesis by using the hydrogen as a reducing agent for carbon dioxide to boot.

4 For the Future

The big victory is somewhere still in the future, but the principles of green chemistry can serve the industry well in some way at all scales. The most elegant and interesting may be in the specialty, fine or pharmaceutical area, but solid, if unobvious contributions have been and will be made in commodities as well.

Acknowledgement

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Notes

1 In 2011, Dow and Mitsui announced a project to produce 320,000 MT ethylene and ultimately polyethylene, from 720,000 m^3 ethanol. This plant would require over 100,000 ha (250,000 acres, ca 400 sq mi) sugarcane production. (Dow-Mitsui Investor Relations Presentation). In 2013, the polyethylene plant was put on hold, with ethanol production still planned. There are few ethanol-to-ethylene facilities, although one owned by Braskem in Brazil is said to be cost competitive with a (relatively expensive) naphtha-based plant. Bio-based polyethylene is said to command a "premium of 40 % or more from clients eager for an enviro-marketing edge." Plastics News, January 10, 2013, http://www.plasticsnews.com/article/20130110/NEWS/301109988/dow-and-mitsui-postpone-sugarcane-polymer-plant. Accessed September 27, 2015

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