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Toward concise metrics for the production of chemicals from renewable biomass

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ABSTRACT

The development of a set of sustainability metrics for quickly evaluating the production of commodity chemicals from renewable biomass is described. The method is based on four criteria: material and energy efficiency, land use and process economics. The method will be used for comparing the sustainability of the production of seven commodity chemicals – lactic acid, 1-butanol, propylene glycol, succinic acid, acrylonitrile, isoprene and methionine – from fossil feedstocks (crude oil or natural gas) versus renewable biomass.

1. Introduction: Origins and definitions

Green chemistry can be succinctly defined as [1]:

> Green chemistry efficiently utilises (preferably renewable) raw materials, eliminates waste and avoids the use of toxic and/or hazardous solvents and reagents in the manufacture and application of chemical products.

It consists of three components: (i) minimization of waste through efficient utilization of mass and energy as raw materials, (ii) avoiding safety and environmental issues associated with the use of toxic and/or hazardous substances and (iii) using renewable feedstocks instead of non-renewable fossil resources in the form of crude oil, coal or natural gas. The guiding principle is the *design* of environmentally benign products and processes (*benign by design*) as embodied in the twelve principles of Green Chemistry formulated by Anastas and Warner [2]. Green chemistry is primary pollution prevention rather than end-of-pipe, waste remediation. It is noteworthy, however, that the concept of green chemistry, in contrast to sustainability, does not contain an economic component. The Brundtland report, *Our Common Future* [3], which recognized the need for sustainable industrial and societal development, defines sustainability as:

> Meeting the needs of the present generation without compromising the needs of future generations to meet their own needs.

In other words, our natural resources should not be used at rates that result in their depletion and residues should not be generated at rates that preclude their assimilation by the natural environment. The concept comprises the so-called three pillars of sustainability: people, planet and profit or social, environmental and economic components. To be sustainable in the long term a technology must satisfy the criteria based on these three components, where green chemistry can be viewed as an enabling technology.

2. The metrics of greenness and sustainability

As Lord Kelvin observed: “to measure is to know”. In order to know if a process is green and sustainable we must be able to measure greenness and sustainability. There is no absolute greenness, however, one process or product is greener than another one, that is there are many shades of green. The most widely accepted measures of the environmental impact of chemical processes are the two most simple metrics: the *E factor* [4,5] defined as the mass ratio of waste to desired product and the *atom economy* [6] or atom utilization, defined as the molecular weight of the desired product divided by the sum of the molecular weights of all substances produced in the stoichiometric equation, expressed as a percentage. A knowledge of the stoichiometric equation allows one to predict, without performing any experiments, the theoretical amount of

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waste that can be expected. Atom economy is a theoretical number that assumes a chemical yield of 100% using exactly stoichiometric amounts of reactants, disregarding excess amounts of reagents used and process aids, such as solvents and acids or bases used in downstream processing, which do not appear in the stoichiometric equation.

The *E* factor, in contrast, is the actual amount of waste produced in the process, defined as everything but the desired product. It takes the chemical yield into account and includes all reagents, solvents losses, process aids and, in principle, even the energy required as this generates waste in the form of carbon dioxide. In the original *E* factor concept water was excluded but there is a definite trend, in the pharmaceutical industry at least, to include water in the *E* factor. A higher *E* factor means more waste and, hence, greater negative environmental impact. In the production of biobased chemicals it is the upstream part, the agriculture itself, that consumes large quantities of water. However, water use can be very different depending on location and on the crop that is grown. For example, corn, requires 300 kg of water to produce 1 kg of plant dry weight, while other crops, e.g. luzerne require up to 800 kg [7]. Furthermore how should we compare places in the world where water is abundant with locations where water is scarce, even for food uses? Hence, we have chosen not to include water use in our concise sustainability metrics.

The *E* factor has been widely adopted by both the chemical and allied industries [8] and academia [9] as a simple and useful metric for quickly assessing the environmental impact of manufacturing processes. Other metrics have been proposed [10–12]. *Reaction mass efficiency* (RME), for example, is a refinement of atom economy that takes the chemical yield of the product and the actual quantities of reactants used into account and the analogous *carbon efficiency* (CE) takes only carbon into account. *Mass intensity* (MI) is defined as the total mass of materials used in a process divided by the mass of product obtained, i.e. MI = *E* factor + 1 and the ideal MI is one [13]. The ideal *E* factor, in contrast, is zero which is a better reflection of the goal of zero waste. Atom economy and *E* factors are complementary; the former being a quick tool that can be used before conducting any experiments and the latter a true measure of the total waste formed in practice.

A limitation of both atom economy and the *E* factor is that they are concerned only with mass efficiencies. However, the environmental footprint of waste is determined not only by its amount but also by its nature. Hence, the term *environmental quotient*, EQ, corresponding to the product of the *E* factor and an arbitrarily assigned unfriendliness multiplier, Q, was introduced [14]. For example, one could arbitrarily assign a Q value of 1 to NaCl and, say, 100–1000 to a heavy metal salt, such as chromium, depending on its toxicity, ease of recycling, etc. Although the introduction of the EQ concept pointed in the right direction there was a definite need for a 'quantitative assessment' of the environmental impact of waste. Consequently, over the last decade, several groups have addressed the problem of quantifying Q. This generally involves an integration of mass efficiency metrics, such as the *E* factor, with *Life Cycle Assessment* (*LCA*) metrics [15]. The latter are used to assess the environmental impact and sustainability of products and processes within defined boundary limits, e.g. cradle-to-gate, gate-to-gate and cradle-to-grave, on the basis of quantifiable indicators, such as energy use, global warming, ozone depletion, acidification, eutrophication, smog formation, and ecotoxicity.

Eissen and Metzger [16], for example, developed the EATOS (Environmental Assessment Tool for Organic Synthesis) software, which can be downloaded free of charge. They used metrics related to health hazards and persistence, bioaccumulation and ecotoxicity to determine the environmental index of the input (substrates, solvents, etc.) and output (product and waste). The outcome is equivalent to EQ in that it constitutes an integration of the amount of waste with quantifiable environmental indicators based on the nature of the waste. It was also possible to introduce the cost of raw materials into the assessment. At about the same time, Saling and coworkers at BASF developed *eco-efficiency analysis* [17,18], based on assessing possible effects of products and processes on human health and the environment and their costs from cradle-to-grave. The goal of eco-efficiency analysis is to quantify the sustainability of products and processes for use as a tool in decision-making processes. Similarly, Jessop and coworkers [19] used a combination of nine LCA environmental impact factors in a gate-to-gate assessment of the greenness of alternative routes to a particular product.

Patel and coworkers [20], building on earlier work of Sugiyama et al. [21], recently described a methodology for the relatively quick assessment of the sustainability of chemical processes in the laboratory stage, based on green chemistry principles, techno-economic analysis and some elements of life-cycle assessment. The method was primarily targeted at evaluating processes for the conversion of biomass into liquid fuels and commodity chemicals by combining quantitative information regarding the raw materials and the process with qualitative indicators reflecting the sustainability of the process. Specifically, it comprised the following five parameters: economic constraints, environmental impact of raw materials, costs and environmental impact of the process, an environmental, health and safety (EHS) index and risk aspects. Basic reaction data was used in conjunction with other information such as physical and chemical properties of the materials, the cumulative energy demand (CED), greenhouse gas emissions (GHG) and commercial availability. The method was used to compare bioethanol-based versus naphtha-based butadiene.

Another approach to compare the efficient use of raw materials in the future might be to assess the energy efficiency in chemical processes. Here we should not only include the fossil energy which always has been available abundantly at low cost, but also we should look at the efficient use of even renewable energy sources. That is why we included this in our metrics.

3. Commodity chemicals from renewable biomass

In addition to minimizing waste generation and avoiding the use of toxic and/or hazardous substances, another important goal of green chemistry and sustainability is the substitution of non-renewable fossil resources – oil, coal and natural gas – by renewable biomass as the primary feedstock for the production of commodity chemicals. Indeed, harnessing the energy of the sun in the synthesis of chemicals, from carbon dioxide and water as the basic raw materials, is surely the quintessence of green and sustainable organic synthesis. The production of fossil resources, in the form of coal, oil and gas, involves such a process but, unfortunately, one that takes millions of years to complete and these resources are being consumed at an unsustainable rate. Mitigation of the depletion of (cheap) fossil resources and the associated global climate change together with the strengthening of rural economy are major drivers in the switch from non-renewable fossil resources, such as oil, natural gas and coal, to renewable biomass. Indeed, biomass is the only renewable energy resource that can also act as a feedstock for chemicals and materials. The key to obtaining an optimum return on investment is to coproduce a range of platform chemicals and materials, in addition to biofuels, in integrated biorefineries [22]. This will also involve second generation bio-based fuels and platform chemicals derived from lignocellulosic biomass and inedible oilseed crops or algal oil as feedstocks [23,24] because of the debate whether or not the use of first generation feedstocks, such as maize and edible oil seeds should be regarded as a sustainable option as it competes, directly or indirectly, with food production. However,