CHAPTER 1

Sustainability of Green Synthetic Processes and Procedures[†]

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1.1 Development and Definition of Green Chemistry

Green chemistry emerged in the 1990s to address the increasing number of health and environmental issues caused by hazardous chemicals and materials.[1] Their toxicity was either not considered or underestimated and sometimes even just simply ignored by some of the stake holders. The eco-toxicology of chemicals had received even less attention until the negative environmental and health effects of dichlorodiphenyl-trichloroethane, DDT, were reported by Raphael Carson in 1962.[2] The number of serious environmental and health problems has rapidly increased in the second half of the last century, mostly due to the frantic expansion of the chemical, petrochemical, and pharmaceutical industry to supply all the goods

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and services for better quality of life of the growing population, as well as to generate more and more profits at the expense of the environment and population.[3] Some of the worst examples include the addition of tetraethyl lead to gasoline,[4] use of thalidomide by pregnant women,[3b] utilization of chlorofluorocarbons (CFCs) in refrigerators,[5] deadly accidents involving dioxins[3b] and methyl isocyanate,[3b] and contamination by crude oil,[6] dioxins,[3b] melamine,[7] and ammonia,[8] just to name a few. The emission of nitrogen oxides above the regulation level by hundred thousands of cheating cars for almost a decade[9] shows that profit making has remained more important than sustainability. While some of these health and/or environmental problems were the result of limited or lack of knowledge on toxicity, bioaccumulation, and ecotoxicity, others were simply due to fraudulent practices, individual or corporate greed, or both.

Environmental and health problems became so visible by the middle of the 1980s that the US Environmental Protection Agency switched the focus from 'end-of-the-pipe clean-up' approach to 'pollution prevention', which led to the enactment of the 1990 Pollution Prevention Act by the United States Congress.[10] In 1995, the traditional blue colour of the cover of *Chemical Reviews*, one of the flagship journals of the American Chemical Society, was changed to green for the one issue dedicated to environmental chemistry.[11] The editorial included one of the earliest published definitions of green chemistry: "It is no longer sufficient to make marvellous new molecules solely on the basis of their marketable properties. Although marketability is an appropriate goal, we, as scientists, must also be concerned with our creations' potential for environmental impact". The publication of the book entitled 'Green Chemistry: Theory and Practice' by Anastas and Warner in 1998 provided a carefully drafted definition: "*Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and applications of chemical products*".[12] The prevention of the environmental and health impacts of hazardous chemicals, materials, and practices is addressed by the 12 principles of green chemistry (Box 1.1).

It should be emphasized that the simultaneous application of several principles of green chemistry for the design of a molecule, a material, a reaction, or a process has been mostly straightforward, but the utilization of all twelve of them is rather difficult, if not impossible. The definition and the twelve principles of green chemistry have not been challenged in the last thirty years, indicating their abiding nature.

1.2 Development and Definition of Sustainability

Sustainability has been the center of attention of humans for a long time, mostly focusing on how to ensure survival, individually or of smaller or larger communities, under sometimes dramatically changing social and environmental conditions. Although the overall achievements of the human race have been spectacular, the rapid development of modern

Box 1.1 The twelve principles of green chemistry[12]

1. It is better to prevent waste than to treat or clean up waste after it is formed.
2. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. Wherever practicable, synthetic methodologies should be designed to use and generate substances that process little or no toxicity to human health and the environment.
4. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. The use of auxiliary substances (*e.g.*, solvents, separation agents, *etc.*) should be made unnecessary wherever possible and, innocuous when used.
6. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. A raw material of feedstock should be renewable rather than depleting wherever technically and economically practicable.
8. Unnecessary derivatization (blocking group, protection and deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible.
9. Catalysts (as selective as possible) are superior to reagents.
10. Chemical products should be designed so that, at the end of their function, they do not persist in the environment and break down into innocuous degradation products.
11. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. Substances and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosion, and fires.

society as well as globalization has had a very negative impact. It was already recognized in 1798 that the faster and faster growing population could surpass sufficient food production resulting in famine, plagues, and even war.[13] The environmental conditions and the future of the habitat of the Earth became worrisome to many by the last quarter of the last century.

In response to the increasing environmental and health concerns, the United Nations has created the World Commission on Environment and Development (or the Brundtland Commission)[14] to formulate a global agenda for change. Their report stated that "*humanity has the ability to make development sustainable to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs*".[15] This definition has been used globally since 1987 and the overarching requisite that 'the needs of the future generations' can be predicted correctly has not been challenged in the last three decades. Although short-term needs can be identified with higher and higher certainty, long-term predictions are still unreliable due to the end of history illusion[16] and the extremely fast advances of science and technology.[17] Consequently, 'sustainability' has been regularly replaced with 'suitability' by many stake holders with vested or conflicts of interests.

It should be acknowledged that, despite the poor definition of sustainability, the worldwide recognition of several adverse environmental or health issues resulted in successful local and global responses. For example, the phasing-out of CFCs as refrigerants to eliminate the cause of ozone depletion or the ban of tetraethyl-lead as an antiknock agent was achieved efficiently. The recently discovered widespread pollution by micro- and nano-plastics is now spurring the global community including scientists and engineers to find efficient solutions.[18]

Although our track record for predicting economic changes or societal transformations has been unreliable, most next-generation definitions and metrics have combined ecological, economical, and societal components at different portions. For example, Robèrt *et al.* have suggested four system conditions as the first order principles for sustainability:[19] (1) *Substances from the lithosphere must not systematically increase in the ecosphere*, (2) *substances produced by society must not systematically increase in the ecosphere*, (3) *the physical basis for the productivity and diversity of Nature must not be systematically deteriorated*, and (4) *fair and efficient use of resources with respect to meeting human needs*. While the first three system conditions may be measured and analyzed, the fourth one, especially the 'fair use of resources' is subjective and probably impossible to define. Another approach proposed the use of the thermodynamic concept of '*lost work*' to address the sustainability of the processing industry: "*Sustainability in the ecological sense means that we do not place an intolerable load on the ecosphere and that we maintain the natural basis for life*".[20] In addition, "*sustainability implies utilization of renewable resources such as biomass or solar energy*". Since the processes converting natural resources to consumer materials and heat do not proceed ideally, part of the work-potential of primary materials is lost and may be the subject of exergy analysis. Another definition demanded that "*sustainable technology must be as efficient as possible and the production of harmless (waste) products may not exceed the assimilative uptake rate of these products in the ecosphere*".[21] The last two definitions have subjective terms such as 'intolerable load' or 'assimilative uptake rate', which would be difficult to define and measure. Sikdar's definition is even more complicated by combining environmental, economic, and societal aspects: "*Sustainability occurs when the material and social conditions for human health and the environment are maintained or improved over time without exceeding the ecological capabilities that support them*".[22] The term 'social conditions' could be rather fuzzy and its measurement could be very subjective again.

In 2015, even the United Nations acknowledged the problem of the ambiguous definitions of sustainability by identifying 17 sustainable development goals (SDGs) and 169 targets.[23] These were the result of the work of hundreds of organizations and thousands of individuals of many countries with significantly different environmental, societal, economic, and political conditions and, more importantly, vastly different short and long term needs and visions. Although the progress of the 17 SDGs will be monitored by the relevant 100 Potential and Indicative SDG Indicators and 152 Complementary National Indicators,[24] neither sustainable development nor its three dimensions were defined. Instead, circular reasoning was used repeatedly by beginning with sustainability to end up with sustainability. For example, "We envisage a world in which every country enjoys *sustained*, inclusive, and *sustainable* economic growth and decent work for all. A world in which consumption and production patterns and use of all natural resources – from air to land, from rivers, lakes, and aquifers to oceans and seas – are *sustainable*".[23b] Thus, the UN's 17 SDGs and the associated targets may serve as a 'roadmap to happiness', but not as a definition to develop metrics to set deliverables and achieve accountability and credibility.

Owing to said ambiguous definitions, 'sustainability' has been regularly replaced with 'suitability' by many stake holders with vested or conflicts of interests to make profits for businesses, secure financial sponsorships for non-governmental organizations and environmentalists, and attract support for politicians and political organizations to be elected or re-elected. In order to prevent the possibility to call 'suitable development' sustainable, sustainability must be defined as an intrinsic property of a molecule, a material, a reaction, a process, a technology, a house, a city, a country, a planet, *etc.* We have recently suggested an alternative simple definition, which is based on the intrinsic evolutionary rules of Nature and independent of the randomly changing economical and societal structures: *Nature's resources, including energy, should be used at a rate at which they can be replaced naturally, and the generation of wastes cannot be faster than the rate of their remediation by Nature*.[25] It is important to recognize that Nature sets the upper limits for the replacement of resources and remediation of wastes, which of course could depend on the geological location and season of the year. This definition is similar to the first two principles, or system conditions, of the four sustainability principles by Robèrt *et al.*[19] It should also be noted that sustainability can be increased by using sustainable repairing, reconditioning, remanufacturing or recycling methods, processes, and technologies. The integration of the use of energy, chemicals, and materials could increase the overall sustainability locally and globally, as both the resource demand and proportional waste generation could be reduced.

1.2.1 Definition of Sustainable Chemistry

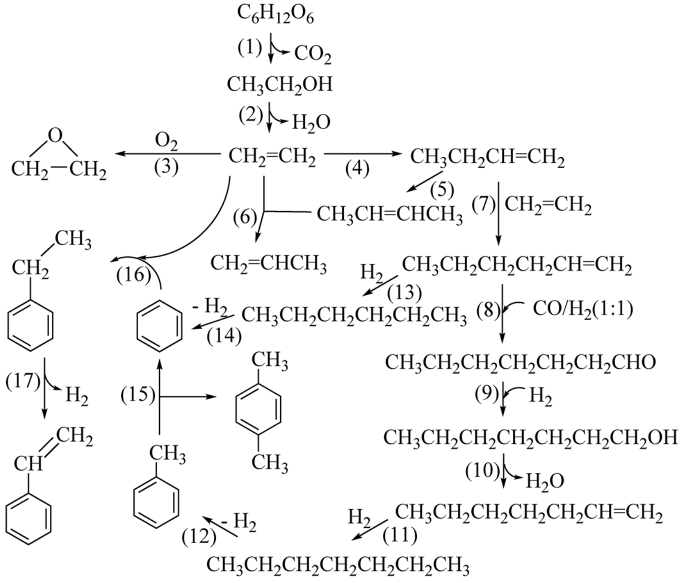
Since some parts of green chemistry may not be sustainable at all, a definition of sustainable chemistry should be established and applied for the assessment of each chemical reaction or process. Based on the definition of sustainability,[25] it was proposed that "*sustainable chemistry should use* *resources, including energy, at a rate at which they can be replaced naturally, and the generation of waste cannot be faster than the rate of their remediation*".[26] It should be emphasized that, according to this definition, all fossil resources cannot be sustainable! Natural gas, crude oil, and coal have been used at a rate much faster than their natural replacement.[27] While their formation requires hundred millions of years, fossil resources will be exhausted in a few hundreds of years. Furthermore, the photosynthesis (Scheme 1.1) is slower than the generation of carbon dioxide and water evidenced by the increasing carbon dioxide levels in the atmosphere from 315 ppm in 1955 to 411 ppm in 2019.

Consequently, a sustainable future requires all carbon chemicals to be produced from carbon dioxide or biomass to achieve a net zero carbon footprint. The easy conversion of polysaccharides to monosaccharides has opened the door for the fermentation to bioethanol (Scheme 1.2, step 1), which can be used as a sustainable resource to produce basic and intermediate chemicals (Scheme 1.2, steps 2–17).

Finally, it should be noted that not all sustainable chemicals or reactions/processes can be green. Therefore, the selection of chemicals, reactions, and processes sustainable and green at the same time should be preferred or the target of future design and innovation.

$$6\,CO_2 + 6\,H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6\,O_2$$

Scheme 1.1 Photosynthesis of C_6-monosaccharides and oxygen.



Scheme 1.2 Biomass-based production of basic carbon chemicals.

1.3 Metrics for Chemistry

The simplest measure of a chemical reaction is the *conversion* of the reactant(s), which shows the level of transformation of the reactant(s) but does not reveal the amount of product(s) and side product(s). The ideal performance of a chemical reaction can be described by the *theoretical yield*, which is the formation of the maximum amount of product(s) in a chemical reaction or process according to the corresponding stoichiometry. The latter is based on the law of conservation of mass, *e.g.*, the total mass of the reactants must equal the total mass of the products and side products. While some reactions can be described theoretically by a chemical equation leading to a single product (*e.g.*, isomerization and addition reactions), others result in two or even more products (*e.g.*, substitution and elimination reactions). It is important to emphasize that the *theoretical yield* requires 100% *conversion* of the starting substrate(s) to the product(s), which is only possible when the *selectivity* of the reaction, the ratio of the desired product(s) to the converted reactants, is 100%. The actual *yield* of a reaction is generally lower than the *theoretical yield* due to low reaction rates (*e.g.*, incomplete reaction) and the simultaneous occurrence of side reactions resulting in side products formed from the starting substrate(s) or secondary products formed from the desired products or side products. The *yield* of product(s) can thus be simply calculated using the *conversion* and *selectivity* (eqn (1.1)):

$$\text{Conversion}(\%) = \frac{\text{Converted reactants}(\text{mol})}{\text{Reactants}(\text{mol})} \times 100$$

$$\begin{aligned} \text{Selectivity}(\%) &= \frac{\text{Desired product }(\text{mol})}{\text{Converted reactants }(\text{mol})} \times 100 \\ \text{Yield}(\%) &= \frac{\text{Conversion}(\%) \times \text{Selectivity}(\%)}{100} \end{aligned} \tag{1.1}$$

A much more realistic measure is the *isolated yield*, which accounts for all the losses during isolation procedures and only considers the isolated moles of the desired products. While these metrics are simple and have been used for a long time, they do not account for all the required chemicals/materials and make it difficult to design and select greener chemical systems.

1.4 Metrics for Green Chemistry

The concept of ecological footprint[28] was developed to understand the human impact on Earth by measuring the consumption of the resources provided by the ecosystem, including the production of goods, services, and some waste remediation capabilities as well. Although determination of the carbon footprint is a well-accepted metric in chemical enterprises, it has been rarely applied for the characterization of chemical reactions, processes, products, and materials. The two most popular metrics, Trost's *atom economy*[29] (which is identical to Sheldon's *atom utilization*[30]) and Sheldon's *environmental factor*,[31] have been developed for green chemistry to provide measurable and verifiable mass balances of chemical reactions and processes at the molecular level. By using the same chemical equations, those needed to calculate the theoretical yield, one can also calculate the *atom economy* or *atom utilization* of the reaction, *e.g.*, how many of all the atoms in the reaction are part of the product(s) (eqn (1.2)). While the *atom economy* of isomerization and addition reactions is 100% theoretically, substitution and elimination reactions are intrinsically dependent on the size of the side products. The *atom economy* or *atom utilization* is of course very useful at the design stage in the development of new chemical processes to select the greenest reactions and minimize waste.

$$\text{Atom economy}(\%) = \frac{\text{Molar mass of products}}{\text{Molar mass of all reactants}} \times 100 \qquad (1.2)$$

The major shortcoming of the *atom economy* is that it does not show all the chemicals and materials required to perform a chemical reaction or process. Various auxiliary substances (solvents, additives, reagents, *etc.*) can be used during the workup of the reactions to ensure the highest yield of the product(s), which in general will become un-recyclable waste. The *Environmental* or *E-factor* was defined to account for all chemicals and materials involved by calculating the ratio of the mass of all wastes per mass of the product(s) (eqn (1.3)).

$$\text{E} - \text{factor} = \frac{\text{Mass of all wastes}}{\text{Mass of products}} \qquad (1.3)$$

For example, Jamison *et al.*[32] demonstrated that E-factors can be significantly reduced by using continuous-flow chemistry,[33] computational calculations, and solvent minimization. The E-factor for the synthesis of atropine was lowered from 2245 to 24, and that for the synthesis of diazepam was reduced from 36 to 9. Several other green metrics have been critically reviewed recently,[34,35] including the carbon efficiency, effective mass yield, mass intensity, reaction mass efficiency, stoichiometric factor, and solvent and catalyst environmental impact parameter.

1.5 Metrics for Sustainability

The exact meaning of the definition of sustainable development by the World Commission on Environment and Development is very subjective and the corresponding goals and deliverables could be markedly different from person to person, city to city, and country to country. Consequently, more than five hundred approaches have been suggested for the measurement of sustainability,[36] most of which were based on the three major dimensions of sustainability at different ratios.[21,37–39] The one-dimensional metrics can be classified as environmental, economic, and social indicators. Two-dimensional metrics combine environmental-social, environmental-economic, and social-economic indicators, and three-dimensional metrics can be obtained from the intersection of the environmental, economic, and social dimensions. Even four indicators, including the material intensity, energy intensity, potential chemical risk, and potential environmental impact can be used for a wide range of process systems.[40]

1.5.1 Ethanol Equivalent

The cost of fossil resources may become so high in the future that carbon chemicals and renewable energy will be produced from biomass. A new metrics called the Ethanol Equivalent (EE) was recently defined to evaluate the sustainability of biomass-based chemicals and energy.[25] The EE is "the mass of ethanol, expressed in million tons ethanol equivalent or MtEE, needed to deliver the equivalent amount of energy from a given feedstock using energy equivalency or produce the equivalent amount of mass of a carbon chemical using molar equivalency". Since the required energy for transportation, storage, mixing, heating, cooling, *etc.* of a given process can also be calculated, the EE of a complete production process or even a total technology can be estimated. The EE has been successfully used as a translational tool between fossil- and biomass-based feedstocks, products, processes, and technologies. Since the EE can be produced by different biomass-based technologies, the required mass of a possible biomass feedstock, the size of the corresponding land, and even the required volume of water can be calculated.

EE calculations are based on first-generation corn-based bioethanol technology commercially practiced in the USA in 2008,[41] including the well-known overall equation of photosynthesis for the production of corn (Scheme 1.1),[42] followed by its conversion into bioethanol by fermentation (Scheme 1.2, step 1) using established technologies. The reason for selecting corn as the biomass, bioethanol as the biomass-based feedstock, and the year 2008 as the reference year was to allow the use of reliable data supported by long-term commercial experience.[43] The used and available resources in the USA in 2008 are listed in Table 1.1.

It is important to note that, in a sustainable world, the energy requirements for the production of ethanol from biomass should also be produced from ethanol. Therefore, the real ethanol equivalent (EE_x) should be used, which also includes the use of one unit of bioethanol to produce x units of bioethanol. For example, when one unit of ethanol was used up for fertilizers,

Table 1.1 Used and available resources in the USA in 2008.

	Units	2008
Crude oil consumption	Million tons oil equivalent	884.5
Natural gas consumption	Million tons oil equivalent	600.7
Coal consumption	Million tons oil equivalent	565
Total fossil resource consumption	Million tons oil equivalent Exajoules	2050.2 86.1
Bioethanol production	Million tons	27.5
Corn production	Million tons	308
Total cornfield (planted corn)	Million hectares	78.6
Total planted land	Million hectares	132
Total land	Million hectares	916
Actual irrigated land	Million hectares	22

powering the farming machinery, fermentation, distillation *etc.*, the estimated return was 2.3 units of ethanol in 2008. Thus, the abbreviation $EE_{2.3}$ means a 2.3 output/input bioethanol ratio or efficiency.

The $EE_{2.3}$ was first used for the evaluation of biomass-based production of gasoline, jet fuel, and basic carbon chemicals, including ethylene, propylene, toluene, xylenes, styrene, and ethylene oxides. The role of $EE_{2.3}$ was similar to the use of million tons of oil equivalents (Mtoe) for coal, crude oil, and natural gas. Accordingly, the $EE_{2.3}$ values of fossil resource-based energy products and carbon-based basic chemicals are summarized in Table 1.2. The $EE_{2.3}$ values of the reaction enthalpies for the production of carbon-based chemicals are based on the heat of formation of the components of the overall reactions from ethanol to the product.

The replacement of 387 million tons of gasoline used in 2008 would have required the production of 808 million tons of $EE_{2.3}$. The proportional corn demand would have been 2739 million tons, about ten-times greater than the actually harvested 308 million tons of corn. Since almost 31% of the total land or 214% of the farmed land of the US would have been needed to grow such 2739 million tons of corn, the use of biomass-based gasoline cannot be sustainable. The replacement of 73.4 million tons jet-fuel with 152 million tons bioethanol on the other hand would only require about half of the currently farmed land, which could be reduced to a sustainable level by the development of more efficient technologies. It should be emphasized that the sustainability of biofuels depends on 'resource availability' since the rate of natural replacement of the resource (*e.g.*, corn *via* photosynthesis) is about a year and the rate of depletion (*e.g.*, burning the biofuel to produce energy, carbon dioxide, and water) is in the range of days to months. Theoretically, the catalytic dehydration of ethanol to ethylene could be sustainable; 54.91 million tons bioethanol could cover the production of 22.5 million tons of ethylene. The production of 14.8 million

Table 1.2 Required $EE_{2.3}$, corn, and land to supply the total demand of gasoline, jet fuel, and several carbon-based basic chemicals from bioethanol in 2008.

	Used in 2008	$EE_{2.3}$	$EE_{2.3}$ of the reaction enthalpy of production	Sum of $EE_{2.3}$	Required corn to produce sum of $EE_{2.3}$		Required land to produce corn by first-generation bioethanol technology in the US in 2008		
Units	Million tons	Million tons	Million tons	Million tons	Million tons	% of total corn	Million hectares	% of land	
								Total	Farmed
Gasoline	387	808	n/a	808	2739	890	283	30.9	214
Jet fuel	73.4	152	n/a	152	514	167	53.2	5.8	40.7
Ethylene[a]	22.5	53.2	1.71	54.91	187.0	60.77	19.36	2.11	14.81
Propylene[b]	14.8	34.8	0.13	34.93	118.3	38.44	12.25	1.34	9.37
Toluene[c]	3.13	7.86	−0.02	7.84	26.51	8.62	2.75	0.30	2.10
Xylenes[d]	5.41	13.47	−0.1	13.37	45.21	14.69	4.68	0.51	3.58
Styrene[e]	4.1	10.42	0.13	10.55	43.40	14.10	4.49	0.49	3.44
Ethylene oxide[f]	2.9	4.36	0.71	5.07	17.69	5.75	1.83	0.20	1.40

[a] Ethanol → ethylene + H_2O.

[b] 3 Ethanol → 2 propylene + $3H_2O$.

[c] 7 Ethanol → 2 toluene + $7H_2O + 6H_2$.

[d] 4 Ethanol → 1 xylene + $4H_2O + 3H_2$.

[e] 4 Ethanol → 1 styrene + $4H_2O + 4H_2$.

[f] 2 Ethanol + O_2 → 2 ethylene oxide + $2H_2O$.

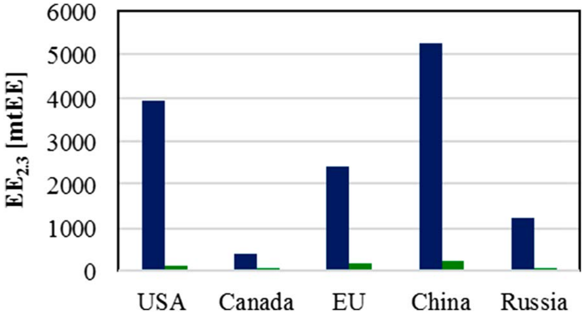


Figure 1.1 $EE_{2.3}$ of total fossil (blue) and renewable (green) energy in 2014. Reproduced from ref. 44 with permission from American Chemical Society, Copyright 2018.

tons propylene, the second largest volume basic chemical, requires 34.9 million tons bioethanol. The volumes of the rest of the basic chemicals in Table 1.2 are much lower.

The sustainability of the replacement of natural gas, crude oil, and coal with corn-based bioethanol was assessed by using ethanol equivalents of fossil resources used in the USA, Canada, EU, China, and Russian Federation in 2008–2014 (Figure 1.1).[44] Based on the $EE_{2.3}$ values, the required volume of corn and the corresponding size of land were calculated, and compared to the actual land used for corn production, which was only enough to replace one sixth of fossil resources in the USA, EU, and China, and practically insufficient in Canada and the Russian Federation. Until the utilization of electricity becomes practical and economical in aviation, biomass-based liquid fuels could be a sustainable alternative.

The 'ethanol equivalent' concept was also used in the development of a novel metric to evaluate the sustainability of carbon-based chemicals.[45] The *sustainability value of resource replacement* (SV_{rep}) and *sustainability value of the fate of waste* (SV_{waste}) were defined and used to establish a *sustainability indicator* (SUS_{ind}) to assess the overall sustainability.

The sustainability value of resource replacement (SV_{rep}) was defined to calculate how much of the necessary resources ($EE_{\text{necessary resource}}$) consumed during a given time ($t_{\text{consumption}}$) can be replaced in a given time ($t_{\text{replacement}}$) by using available biomass-based resources ($EE_{\text{available resource}}$) and the best replacement technologies, which have measurable effectiveness values (ERoE) (eqn (1.4)). While the $EE_{\text{necessary resource}}$ is the sum of the EE based on carbon-atom equivalency according to the overall yield of production from bioethanol and the EE of the standard enthalpy of the reaction ($EE_{\text{overall standard enthalpy of reaction}}$), the $EE_{\text{available resource}}$ is the total amount of bioethanol available on the market. The measurable effectiveness of the reference technology is characterized by its ethanol return of ethanol or ERoE, which is equal to 2.3 indicating that, out of the total 3.3 units of bioethanol, one unit is required for the production of 2.3 units of bioethanol.[46] Thus, the total $EE_{\text{available resource}}$

has to be multiplied by 2.3/(1 + 2.3) = 0.7 to secure the sustainable production of the resource.

$$SV_{\text{rep}} = \frac{\frac{\text{ERoE}}{1+\text{ERoE}} \times \frac{\text{ERoE}}{2.3} \times EE_{\text{necessary resource}} + EE_{\text{secondary resource}}}{t_{\text{replacement}}} \Bigg/ \frac{EE_{\text{necessary resource}}}{t_{\text{consumption}}} \tag{1.4}$$

Ideally, the available resource should be at least equal to the necessary resource and the amount required to produce the necessary resource during the same time period to avoid either resource shortage or over production leading to storage issues. In general, the amount of resources could be increased by using the same chemical as a secondary resource ($EE_{\text{secondary resource}}$) from another biomass-based technology.

The sustainability value of the fate of waste (SV_{waste}) is defined as one when the continuously produced generated waste ($EE_{\text{generated waste}}$) is equal to the continuously treated waste ($EE_{\text{treated waste}}$) in the same time period ($t_{\text{waste generation}} = t_{\text{waste treatment}}$) and no waste is released to the environment ($EE_{\text{untreated waste}} = 0$ and $t_{\text{waste natural decomposition}} = 0$) (eqn (1.5)). The treatment methods could include incineration, chemical and biological treatments, and disposal to official waste storage sites including landfills. All waste released to the environment must be considered as untreated waste.

$$SV_{\text{waste}} = \frac{EE_{\text{treated waste}} + EE_{\text{untreated waste}}}{t_{\text{waste treatment}} + t_{\text{waste natural decomposition}}} \Bigg/ \frac{EE_{\text{generated waste}}}{t_{\text{waste generation}}} \tag{1.5}$$

The following assumptions have been made: (a) if no waste treatment is applied, the associated EE and time must be equal to zero; (b) the time of natural decomposition of untreated waste should include one year (if waste generation time is assumed to be one year) and the time needed to reach the local government's regulation level in the environment based on its natural half-life; (c) in the case of multi-step technologies with the potential to generate waste in each step, the longest time of natural decomposition should be used for the overall process; and (d) in the case of contamination of air, water, and/or soil, the longest time of natural decomposition should be used. If a side or minor product can be utilized in another technology, it should be considered as a secondary resource and not as a waste. Since the sum of $EE_{\text{treated waste}}$ and $EE_{\text{untreated waste}}$ must be equal to $EE_{\text{generated waste}}$, all waste streams are accounted for. By selecting the longest time for the natural decomposition of untreated waste, the persistent component of the waste with the longest half-life will significantly lower SV_{waste}. In other words, prevention of persistent waste formation by the development of efficient processes or integrated valorization of the waste is the preferred path to reach sustainability.

The sustainability indicator (SUS_{ind}) is based on the sustainability values of resource replacement (SV_{rep}) and sustainability values of fate of waste (SV_{waste}) by merging a two-body issue into a single one (eqn (1.6)).[45]

$$\mathrm{SUS_{ind}} = \frac{\mathrm{SV_{rep}} \times \mathrm{SV_{waste}}}{\mathrm{SV_{rep}} + \mathrm{SV_{waste}}} \tag{1.6}$$

Consequently, sustainability requires that all resources must be replaced ($\mathrm{SV_{rep}} = 1$) and all wastes can be recycled or the remaining parts treated ($\mathrm{SV_{waste}} = 1$) within a specific time. While $\mathrm{SUS_{ind}} \geq 0.5$ indicates equal or better than the required sustainability, $\mathrm{SUS_{ind}} < 0.5$ denotes an unsustainable situation.

In order to demonstrate the applicability of these sustainability metrics, the $\mathrm{SV_{rep}}$, $\mathrm{SV_{waste}}$, and $\mathrm{SUS_{ind}}$ values for ethylene, propylene, toluene, *p*-xylene, styrene, and ethylene oxide were calculated as if they were produced from bioethanol by known reactions and processes (Scheme 1.2) for the consumed quantities in the USA in 2008 (Table 1.3). If these basic chemicals had to be produced from biomass, the total amount of required bioethanol would have been 151.93 million tons, which is significantly over the total bioethanol production of 27.8 million tons. The limited amount of bioethanol was used proportionally for each chemical.

The $\mathrm{SV_{rep}}$ values for these chemicals are between 0.128–0.625 (Figure 1.2) and, therefore, none of them are sustainable. The $\mathrm{SV_{rep}}$ of styrene is much higher than the others due to the utilization of benzene, produced as a side product in the production of *p*-xylenes as a secondary resource. This result indicates that integration of side and waste products could significantly lower the resource demand and increase the sustainability. The $\mathrm{SV_{rep}}$ for these chemicals would be much smaller if we had taken out all the bioethanol burned as gasoline additive.

In order to achieve sustainability, the total available bioethanol volume should be equal or higher than 151.93 million tons. This would require the production of 515 million tons of corn, which would be 1.67 times the 308 million tons of total corn produced in the US in 2008. Subsequently, 53 million hectare land or 40.2% of the total 132 million hectares of farmed land should be used for corn production. Of course, the demand for bioethanol, corn, and arable land would be significantly higher if bioethanol was used as fuel at the same time (since the calculations in this paper used every drop of bioethanol for the production of carbon-based chemicals). One possible approach to secure the required 151.93 million tons bioethanol is to improve the ERoE from 2.3 to at least 18, a formidable challenge on production technologies. Alternatively, the valorization of agricultural residues and food wastes could also contribute significant amounts of bioethanol, not to mention the beneficial effect on waste management in highly populated areas. The $\mathrm{EE_{generated\ waste}}$ for each chemical is based on the EE of wastes in each step shown in Scheme 1.2. The $\mathrm{SV_{waste}}$ values for these chemicals are between 0.48–0.96 (Figure 1.2) and therefore none of them are sustainable. While waste prevention is the best for the dehydration of ethanol to ethylene ($\mathrm{SV_{waste}} = 0.96$), all the other technologies produce significant amounts of waste.

Table 1.3 Sustainability analysis of basic chemicals in the USA in 2008.

	Basic chemicals						
	Ethylene	Propylene	Toluene	*p*-Xylene	Styrene	Ethylene oxide	Σ Chemicals
Produced amount [mt year^{-1}][a,b]	22.5	14.8	3.13	5.41	4.1	2.9	52.84
$EE_{\text{required resource}}$ [mt][c]	37.47	47.26	8.76	49.37	5.62	3.40	151.87
$EE_{\text{overall standard enthalpy of reaction}}$ [mt][d]	1.206	0.177	−0.078	−1.287	0.191	−0.151	0.058
$EE_{\text{neccessary resource}}$ [mt]	38.68	47.43	8.68	48.08	5.81	3.25	151.93
$EE_{\text{proportional necessary resource}}$ [%][e]	25.46	31.22	5.71	31.65	3.82	2.14	100
$EE_{\text{secondary resource}}$ of benzene[f] [mt]	0.00	0.00	0.00	0.00	16.21	0.00	16.21
$EE_{\text{proportional secondary resource}}$ [mt]	0.00	0.00	0.00	0.00	2.89	0.00	2.89
$EE_{\text{available resource}}$ [mt year^{-1}][g]	27.8						
$EE_{\text{proportional available resource}}$ [mt year^{-1}][h]	7.08	8.68	1.59	8.80	1.06	0.59	27.8
$SV_{\text{rep2.3}}$	0.128	0.128	0.128	0.128	0.625	0.128	0.147
$EE_{\text{generated waste}}$ [mt year^{-1}]	0.37	7.62	2.08	12.02	0.17	0.37	22.63
$EE_{\text{recycled waste}}$ [mt year^{-1}]	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$EE_{\text{treated waste}}$ [mt year^{-1}]	0.00	2.70	2.02	11.61	0.00	0.00	16.33
$EE_{\text{untreated waste}}$ [mt]	0.37	4.92	0.06	0.41	0.17	0.37	6.30
$1 + t_{\text{waste natural decomposition}}$ [year]	1.044	1.099	1.044	1.044	1.137	1.601	n/a
SV_{waste}	0.96	0.48	0.49	0.49	0.88	0.62	n/a
SUS_{ind}	0.113	0.101	0.101	0.101	0.365	0.106	n/a

[a] mt = million tons.

[b] The chemical is completely consumed within one year.

[c] Based on carbon-atom molar equivalency of the chemicals and combined yields (conversion × selectivity) of all reactions from ethanol to the chemical.

[d] Overall standard enthalpy of reaction: the sum of each reaction's enthalpy.

[e] $(EE_{\text{neccessary resource}}/EE_{\Sigma\text{Chemicals}}) \times 100$.

[f] The amount of benzene available from xylene and styrene production.

[g] Bioethanol production in the USA in 2018.

[h] $(EE_{\text{neccessary resource}}/EE_{\Sigma\text{Chemicals}}) \times EE_{\text{available resource}}$.

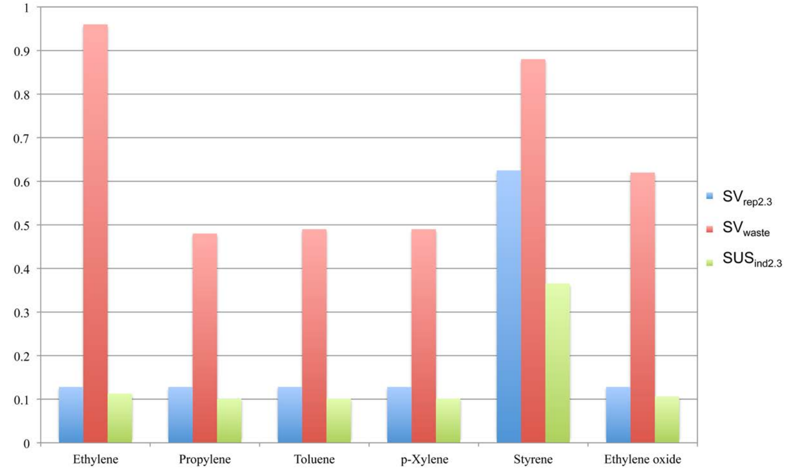


Figure 1.2 Sustainability metrics of basic chemicals in the USA in 2008.

Since the values of SV_{rep} and SV_{waste} are below one, the SUS_{ind} index lies between 0.1 and 0.365 for all these chemicals (Figure 1.2), indicating that none of them are sustainable. Therefore, bioethanol-based carbon products should be labeled 'sustainable' only when the necessary land is available, independently of social and economic changes.

In conclusion, these six basic chemicals cannot be produced sustainably due to the limited availability of bioethanol. However, a ten-fold increase of the volume of bioethanol could easily result in a completely biomass-based production of carbon-based chemicals. The SV_{waste} of the processes is higher than SV_{rep} because of the successful waste prevention and process integration of contemporary petrochemical technologies.

The results suggest that chemical companies could achieve sustainability based on the molar equivalency of the total carbon atoms used by simply owning enough land to produce renewable resources. Of course, the position and size of the lands and the crops produced should be carefully selected to secure sustainable farming and production technologies. Although sustainability may be reached on a molar basis, an additional challenge is to cover the associated energy demand of production processes, storage, and transportation by renewable energy.

1.5.2 Atom Equivalent

The ethanol equivalent-based sustainability metrics are limited to energy and carbon chemicals. In order to expand the applicability of SV_{rep} and SV_{waste} beyond carbon-chemicals, the replacement of EE with the Atom Equivalent (AE) was proposed to represent any elements of the periodic table as constituents of chemicals and materials.[47] The AE is defined as the equivalent mass of one of the constituent elements of a chemical or a material based on molar equivalency. For example, in the case of lithium batteries, the lithium equivalent (LiE) is the mass of all lithium atoms present in a resource, a product, a side-product, or a waste in the form of LiCl, $LiCO_3$, $LiCoO_2$, $LiFePO_4$, $LiMn_2O_4$, Li_2MnO_3, $LiNiMnCoO_2$, $LiNiCoAlO_2$, or $Li_4Ti_5O_{12}$. The energy vector of any given technology must be an intrinsic part of the calculation of SV_{rep}, SV_{waste}, and SUS_{ind}. The calculations will require reference technologies commercially used for years. It should be emphasized that the available resources for any element must be accessible by ecologically sound processes and technologies.

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