

# Green chemistry and the bioeconomy: a necessary nexus

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**Abstract:** Economically viable green chemistry processes are the technology enablers of the bioeconomy. Access to an economically viable green chemistry production route, however, is not *per se* sufficient for successful bioproduction. The cases of synthetic amorphous silica, pectin, polysaccharide nanofibers, pelargonic acid, hydrogen peroxide electrochemically sourced from water, and that of valued bioproducts (orange oil, limonene, and dietary fiber) from fresh orange peel were selected to substantiate these assumptions. The study concludes by identifying three conditions for competitive bioproduction methods, along with learning and educational outcomes considered relevant for green chemistry and bioeconomy educators. © 2024 The Authors. *Biofuels, Bioproducts and Biorefining* published by Society of Industrial Chemistry and John Wiley & Sons Ltd.

**Key words:** green chemistry; bioeconomy; chemical industry; bioproduction; circular economy

## Introduction

Chiefly based around the idea of pollution prevention, green chemistry emerged as a systematic research program around the early 1990s, following the publication, in 1996, of *Green Chemistry: Designing Chemistry for the Environment*,<sup>1</sup> a book collecting the presentations given at a symposium held in 1994 during the 208th national meeting of the American Chemical Society. The symposium focused ‘on environmentally benign chemistry research in the international arena’.

In 2010, Linthorst showed how the historical development of green chemistry could be divided conveniently into three periods.<sup>2</sup> The first, between 1990 and 1993, corresponded to its origins within the Environmental Protection Agency

of the USA following a 1990 federal law on pollution prevention. A second period, between 1993 and 1998, featured a marginal increase in research, and was followed by a third period, between 1999 and 2008, during which a huge growth in research (and government funding) occurred. In 1999, the Royal Society of Chemistry, a key publisher of chemistry research, launched the new journal *Green Chemistry*.

According to Linthorst, green chemistry would be ‘a conceptual framework that can be used in the design of chemical processes achieving environmental and economic goals by way of preventing pollution.’<sup>2</sup> Since the early 2000s, this time essentially in Western Europe, the concept of a ‘bioeconomy’ emerged as the driver of numerous studies, even though no clear definition of it existed.<sup>3</sup>

In the early 2010s, the bioeconomy was defined as the economy in which the raw materials for materials, chemicals, and fuels were derived from renewable biological resources.<sup>3</sup> An expanded definition identifies the bio-based economy as the economy in which chemicals and materials are obtained from biological resources, and energy from renewable energy sources.<sup>4</sup> Indeed, reviewing the history of the bioeconomy, Befort has recently shown how it is rooted in the history of chemistry.<sup>5</sup>

Driven by megatrends concerning the environment, health, and energy that permeate society on a global scale, Pagliaro forecast in 2019 that the chemical industry would shift towards waste-free continuous flow productions carried out in small, flexible plants, preferably using biological feedstock in place of oil-derived feedstock.<sup>6</sup>

Seen from this perspective, failures in commercializing bioproduction would be due to green chemistry production routes being economically unviable, often because they are carried out in batches using cumbersome, multi-step processes, characterized by low productivity, whereas economically viable green chemistry production processes would be the necessary enablers of the bioeconomy. Access to an economically viable green chemistry production route, however, is not *per se* sufficient for successful bioproduction. The cases of synthetic amorphous silica, pectin, polysaccharide nanofibers, pelargonic acid, hydrogen peroxide electrochemically sourced from water, and that of valued bioproducts (orange oil, limonene and dietary fiber) from fresh orange peel, were selected to substantiate these assumptions.

## Green chemistry-enabled bioproduction methods

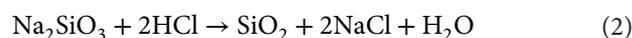
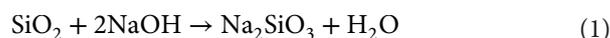
Six new production routes illustrate how economically viable green chemistry technology enables bioproduction methods

that replace wasteful and obsolete multi-step production routes. The examples are summarized in Table 1, which also indicates their green chemistry/engineering features and the benefits offered by the new bioproduction methods.

### Synthetic amorphous silica

In 2023, a large chemical company in Italy<sup>7</sup> and another in Thailand<sup>8</sup> announced the forthcoming production of synthetic amorphous silica (SAS) for automotive tires using sodium silicate derived from rice husk ash (RHA) sourced from rice-milling companies. The silica content in RHA is very high, amounting to 90% along with 5% C and 2% K<sub>2</sub>O.<sup>9</sup> The addition of highly dispersible silica to tire tread reduces fuel consumption by up to 8% in comparison with conventional passenger car tires.

Silica in RHA can be atom-efficiently converted into pure sodium silicate solution, and thus to ultrapure silica following precipitation with acid (Eqns 1 and 2).



Base and acid are used in equal amounts yielding NaCl as a by-product that is collected and sent back to the soda manufacturer to produce new soda. First demonstrated in 2000 obtaining ultrapure silica,<sup>10</sup> the process was scaled-up by an Austrian company that operates a demonstration plant in Germany from 2016.<sup>11</sup> In brief, RHA is first reacted with aqueous NaOH at 90 °C under moderate pressure (≥1 bar) affording a sodium silicate solution with soluble contaminants and undissolved nanoporous carbon particles, which are removed by filtration. The silicate solution is thus concentrated and eventually added with aqueous HCl to precipitate ultrapure SAS and sodium chloride. The latter is recovered and sent back to the soda supplier for NaOH

**Table 1. Selected bioproductions, green chemistry features and benefits.**

Product	Green chemistry/engineering features	Benefit
Synthetic amorphous silica	Rice hull ash feedstock to replace sand, base/acid treatment	Renewable feedstock, lower process temperature
Pectin	Steam flash hydrolysis, ultrafiltration, and diafiltration	Lower mass/energy cost, greater purity, and homogenous products
Polysaccharide nanofibers	Oxidation by immobilized TEMPO	Minimizing the use of TEMPO and toxic waste
Pelargonic acid	New process design: Oxidative cleaving of oleic ester in triglyceride	Renewable feedstock, eliminating the risk of using ozone, reduce mass intensity
Hydrogen peroxide	Direct oxygen reduction with Pt-Hg/C catalyst	On-site production eliminates the risks of transportation and storage
Dietary fiber, orange oil	Green extraction from fresh waste orange peel	Highly valued bioproducts from biowaste, normally landfilled or incinerated

production needed for Eqn 1, thereby closing the material cycle.

The biobased route was commercialized because it enables the replacement of the conventional process for making precipitated silica, in which silica sand is reacted with sodium carbonate at 1300 °C to form sodium silicate glass. This is then dissolved in water and amorphous silica is precipitated by adding one equivalent of sulfuric acid affording sodium sulfate and 1 t CO<sub>2</sub>/t of SiO<sub>2</sub>. The biobased process dramatically lowers the capital expenditure (CAPEX) and operational expenditure (OPEX) making its commercialization economically viable, provided that the RHA used is suitable for silicate production.<sup>12</sup>

## Pectin

Produced industrially since the early 1940s using the acid hydrolysis of dried lemon peel or apple pomace, pectin is the most valued food hydrocolloid.<sup>13</sup> From the early 2000s, demand for it has increased substantially, but the industrial production route employing diluted hot mineral acid (hydrochloric, nitric or sulfuric acid) for the extraction and alcohol for precipitating pectin requires high CAPEX and OPEX.<sup>14</sup> The process produces a large amount of waste in the form of acid-processing water and requires a substantial amount of heat and alcohol, limiting the use of new plants to increase supply and meet the growing demand.

The rapidly expanding pectin market and the high production costs mentioned above create room for new production methods using green chemistry technology. Indeed, much new academic (and industrial) research has focused on the green production of pectin using greener extraction and isolation methods. To improve the extraction of polysaccharides, the use of organic acid in place of mineral acid as well as the use of microwaves, cavitation bubbles, subcritical water, and enzymes has been widely investigated.<sup>15</sup>

Conventional pectin isolation, based on the concentration of pectin solution by evaporation at low pressure and high temperature, followed by the addition of alcohol in 1:3 excess ratio and the recovery, using vacuum evaporation, of a large amount of expensive and flammable alcohol needs to be replaced with green technology. Using a diaultrafiltration process in a pilot system equipped with hollow fiber polysulfone or polyamide membranes with 2 m<sup>2</sup> filtration area to purify and concentrate a 26–28 L hydrolysate solution, Muhidinov and co-workers demonstrated that diaultrafiltration is both a low-cost and green process to isolate pectin of higher purity, higher molar mass and lower polydispersity in comparison with the conventional isolation process.<sup>16</sup> Along with superior bioproduct quality,

the membrane-based isolated process carried out at ambient temperature and moderate (0.8–1.2 bar) inlet pressure requires a quarter of the amount of power and half the amount of ethanol.

## Polysaccharide nanofibers

Nanocellulose is a bionanomaterial with exceptional mechanical, optical, biological, barrier, and textural properties, which, coupled with tunable surface chemistry and low density, will drive applications in widely different industrial sectors,<sup>17</sup> once a production route affording the product in large amount at affordable cost is developed. Industrial applications so far have been limited by the high cost of its multi-step extraction routes involving energy-intensive mechanical treatment of wood pulp followed by treatment with concentrated H<sub>2</sub>SO<sub>4</sub> to obtain cellulose nanocrystals, or chemical oxidation followed by mechanical fibrillation of the partly oxidized fibers.

Amid the new green routes to cellulose nanofiber (CNF) developed between 2011 and 2022,<sup>18</sup> a breakthrough in the industrial production of CNF was reported in 2019 by research chemists based at South Korea's largest chemical company, reporting the one-pot synthesis of CNF from bacterial cellulose using the immobilized TEMPO (2,2,6,6-tetramethyl-1-piperidine-*N*-oxy radical) catalyst, *SiliaCat* TEMPO.<sup>19</sup> The catalyst was found to be easily recyclable after simple filtration, with stable catalyst activity (70% reaction yield after five consecutive reaction runs), whereas residual hypochlorite in solution was entirely removed by the addition of 0.3% ascorbic acid, without washing. This heterogeneously catalyzed, one-pot production route ensures low production costs because the expensive catalyst-product separation and product purification from genotoxic TEMPO steps are no longer required.

The method is general and can also be applied to oxidize wood cellulose fibers, as indirectly shown in 2017 by Renneckar and Patankar, who described the green synthesis of CNF derived from wood pulp fibers using another silica-based sol-gel catalyst, namely the magnetically recoverable Karimi's catalyst (TEMPO@SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub>), followed by the mechanical disintegration of the oxidized cellulose fibers.<sup>20</sup> Like the oxidation mediated by TEMPO in solution, the heterogeneously catalyzed process affords 5 nm thick cellulose nanofibrils, but the catalyst can now be separated from the oxidized nanofibrils using a magnet, and the catalyst recovered can be reused in four consecutive reactions.

The same *SiliaCat* TEMPO catalyst was successfully employed for the one-pot, green synthesis of sacchachitin (a water-insoluble heteropolysaccharide consisting of about 40%

chitin and 60%  $\beta$ -1,3-glucan) nanofibers in 2021 by scholars based in Taiwan.<sup>21</sup> These highly biocompatible nanofibers have shown highly promising results for enhanced diabetic wound healing.<sup>22</sup> In brief, the use of this immobilized TEMPO catalyst shifts the carboxylation process mediated by genotoxic TEMPO in solution to a process mediated by a leach-proof solid catalyst allowing the synthesis of insoluble polysaccharide nanofibers of superior quality, eliminating waste.

## Pelargonic acid

Pelargonic (nonanoic) acid is a broad-spectrum herbicide for drying out weeds quickly leaving no toxic or harmful residues.<sup>23</sup> For decades, it was manufactured by liquid-phase continuous oxidation of *n*-nonanal, an aldehyde obtained by the highly selective and costly hydroformylation of 1-octene or, to a lesser extent, by ozonolysis of oleic acid with harmful ozone. In 2005, however, industrial researchers in Italy described an improved process for the production of saturated fatty acids based on the oxidative scission of oleic acid (9-octadecenoic acid) into pelargonic acid (PA) and azelaic acid (AA) with 30% aqueous H<sub>2</sub>O<sub>2</sub> without the need for an organic solvent, mediated by a catalytic amount of tungstic acid (between 0.08 wt% and 1.5 wt% with respect to oleic acid) at a temperature between 50 and 90 °C at atmospheric pressure.<sup>24</sup> A surfactant is used to disperse the two phases, eliminating the need to add excess water in the hydrolytic step of the reaction of oxidative scission if not the modest amounts of water in the solution in which the catalyst is dissolved.

The process is a green chemistry production route that can be further improved, eliminating the surfactant and using a peroxo-tungsten complex [C<sub>5</sub>H<sub>5</sub>N(*n*-C<sub>16</sub>H<sub>33</sub>)]<sub>3</sub>{PO<sub>4</sub>[W(O(O<sub>2</sub>)<sub>2</sub>)<sub>4</sub>]} as phase-transfer catalyst to transfer the oxidant from the aqueous phase to the organic phase, which is generated *in situ* in the presence of tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) and hydrogen peroxide.<sup>25</sup> In the (Godard) process the catalyst can be recycled once (cold treatment for recovery of the catalyst by filtration) along with the aqueous phase, so only half of the hydrogen peroxide (5 eq., corresponding to the oxidant) is introduced to start the second oxidation, eventually affording excellent 90.1% atom economy and *E* factor ( $m_{\text{waste}}/m_{\text{product}}$ ) of 13 essentially due to the ethyl acetate used to extract PA and AA (followed by vacuum distillation to separate 92% pure PA).

In 2012, the same Italy-based researchers discovered that it is possible to produce saturated monocarboxylic acids starting directly from vegetable oils without the need for preliminary modifications such as the hydrolysis of the

triglycerides comprising the oil.<sup>26</sup> The oil is first reacted at 60–65 °C with 50% aqueous H<sub>2</sub>O<sub>2</sub>, added slowly in the presence of a catalytic amount of tungstic acid for the oxidation reaction of the olefinic double bond of the unsaturated fatty acid. The vicinal diol obtained in this way is then oxidized with pressurized air (12 bar) in the presence of an oxidation catalyst such as an aqueous solution of 1% cobalt acetate, converting the two hydroxyls to carboxylic groups. The aqueous phase contains the catalysts of the first two reaction steps (tungstic acid and cobalt salt) that are subsequently recovered, whereas the organic phase undergoes distillation with quick separation of PA from triglycerides of azelaic acid (further hydrolyzed in glycerol and azelaic acid).

Overall, these green chemistry innovations make the biobased route to pelargonic acid competitive with the petrochemical process.

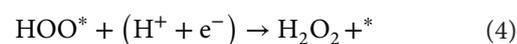
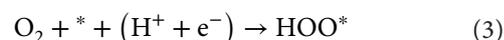
The production of pelargonic acid using the process developed in Italy started in Sardinia in 2014 at a dedicated plant targeting the production of 9.4 kt/year.<sup>27</sup> The latter production rate would be about 23% of the 40 kt/year pelargonic acid global market in 2015, though the company in 2016 estimated that the market, when replacing C8-C10 acids and main commercial herbicide with pelargonic acid, could grow to 1600 kt/year.<sup>28</sup>

The Godard process is also used to manufacture AA used as active ingredient of the first bio-based weed control product (tradenamed Beloukha) authorized for use in EU countries.<sup>25</sup>

## Hydrogen peroxide from water

Since the early 2020s, a company in Denmark has successfully commercialized a line of on-site on-demand electrochemical hydrogen peroxide generators, requiring only water, electricity, and air to operate, affording between 1 and 5 kg/day yields of hydrogen peroxide made available as dilute aqueous solution.<sup>29</sup> Such safe and green production of H<sub>2</sub>O<sub>2</sub> directly from water meets the requirements of most horticulture and livestock applications, as well as for water disinfection and wastewater treatment.

The technology employs the electrochemical two-electron oxygen reduction reaction using a highly active and stable nanoparticulate Pt–Hg/C catalyst in which a catalytic Pt–Hg alloy reproducibly electrodeposited from HgClO<sub>4</sub> on Pt nanoparticles mediates the electroreduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> by two coupled electron and proton transfers (Eqns 3 and 4):<sup>30</sup>



where \* and HOO\* respectively denote an unoccupied active site at the catalyst surface, and the single adsorbed intermediate for the reaction.

The company offers two series of hydrogen peroxide generators, one designed for applications requiring between 1 kg H<sub>2</sub>O<sub>2</sub>/day and up to 3 kg H<sub>2</sub>O<sub>2</sub>/day such as greenhouse irrigation, livestock water treatment, aquaculture hatcheries, and low-throughput industrial and municipal water-treatment plants, that were sold, for example, in late 2023 by intermediaries in the USA between \$28 712 (for the 1 kg/day) and \$40 848 (for the 3 kg/day) systems.<sup>31</sup> Another, designed for applications requiring 5 kg H<sub>2</sub>O<sub>2</sub>/day and above, such as for irrigation water treatment in >50 ha sized fields, mid-size to large cooling towers, advanced oxidation processes, and process water treatment.<sup>29</sup>

Again, it is perhaps not surprising to learn that the company in 2023 received €14 million funding to expand production and meet the rapidly rising demand for on-site production of aqueous hydrogen peroxide using only water and electricity that originates from the pharmaceutical and food and beverage sectors.<sup>32</sup>

‘New chemical production based on advanced catalysis technologies ... starting from readily available biomass raw materials intrinsically leads to decentralized production, located close to customers’<sup>6</sup> wrote one of the authors of the current paper in 2019, attempting to devise forthcoming chemical productions. ‘A common feature of all new catalytic technologies’ is that they will be ‘conducted heterogeneously and under flow, namely in continuous processes over solid catalysts in a continuous flow reactor (a unit that processes many reactor volumes without interruption), affording very limited waste and by-products or none at all.’<sup>6</sup>

## Competitive bioproductions

Nearly always, bioproduction methods will compete with existing chemical production methods, most of which start from oil-derived feedstocks. Low production cost is thus necessary (but not sufficient) for biobased products to be competitive. An economically viable (low CAPEX and low OPEX) green chemistry process allows such lower production costs due to milder reaction conditions and high atom efficiency, resulting in a lack of by-products to be processed.

Two more conditions, however, need to be met to start a competitive bioproduction method (Table 2): a remunerative price of the bioproduct, and reliable, prolonged access to the biobased raw material purchased at affordable price.

For example, around 2005 the price of glycerol from biodiesel and oleochemical productions became so cheap and the feedstock so abundant that it was possible to make

**Table 2. Requirements for competitive bioproductions.**

Requirement	How to achieve it
Low production cost	Green chemistry route
Cheap and abundant biobased raw material	Partnership with suppliers
High bioproduct selling price	Proper selection of end market

the production of the valued substance epichlorohydrin from glycerol highly competitive with that from propene. In detail, the price of crude (80%) glycerol was so low (around €20/t) and that of epichlorohydrin was so remunerative (€1600/t) that a 26.5 kt/year glycerol to epichlorohydrin plant (which affords a tenfold reduction in wastewater generation compared to the propene-based route), yields a 5 year payout time, ensuring substantial profits for the lifetime of the plant, projected to operate for 20 years.<sup>33</sup> Indeed, the technology flourished with several manufacturers of biobased epichlorohydrin. In late 2021, an Austrian engineering company signed a technology and license agreement to supply a glycerol-based epichlorohydrin production 200 000 t/year plant (the world's largest) in China.<sup>34</sup>

Most failures in the biobased chemical industry have been due to bioproduction methods being unable to meet one or more of the above three requirements. Many companies, for example, targeted the production of fuels and commodity plastics (plastic produced in huge volumes for low value end applications such as packaging, food containers, and household products). Others targeted the production of engineering plastics, starting from cheap and abundant raw materials such as molasses or glycerol, but used cumbersome and inefficient fermentation routes in batches whose low productivity made the production cost too high. Those that targeted the production of high-value bioproducts made using atom-efficient production routes, on the other hand, thrived and became part of the new bioeconomy industry.

Low production costs are the necessary condition for a bioproduct to be competitive in the marketplace. Even in that case, access to affordable and reliable biobased raw materials is necessary to establish successful bioproduction. First-generation biorefineries using conventional chemical technology – such as hydrolytic processes using mineral acid with biomass – face large volumes of low value by-products, typically rich in lignin, which intrinsically limits their economic viability. Finally, the bioproduct targeted should have a remunerative price and relatively large demand.

It is not the ‘greenness’ or the low ‘carbon footprint’ that will determine the success of a bioproduction but rather its intrinsic capability to compete in the marketplace with conventional products.

By selecting a biological raw material rich in valued bioproducts and poor in lignin, such as waste orange peel, one company has, since 2021, successfully manufactured orange oil, limonene, and dietary fiber (a natural hydrocolloid made of molecularly intertwined cellulose and pectin fibers).<sup>35</sup>

Dietary fiber, as a by-product, originates from the abundant amount of cellulose in waste lemon (21.1% of cellulose and 7.3% of hemicellulose of dried peel)<sup>36</sup> and orange (9.2% cellulose and 10.6% hemicellulose).<sup>37</sup> In contact with water, this natural fiber acts as hydrocolloid, absorbing a large amount of water at the surface, improving mouthfeel in many foods and beverages while providing firmness and structure to a wide variety of cosmetic and personal care products.

The company currently operates in the Netherlands Europe's largest orange peel factory, where more than 30 000 t of peels are processed yearly using green extraction techniques such as cold pressing and acid-free hydrolysis. Peels are derived from orange peel collected from restaurants, supermarkets, catering companies, and even offices, originating from freshly consumed fruits. Consumers looking for healthier and more natural products, are shifting consumption of orange juice from reconstituted frozen concentrate orange juice to fresh, locally made ('not from concentrate') juice.<sup>38</sup>

Showing evidence of the market value of these bioproducts, the orange oil recovered through cold pressing from waste orange peel is sold online (in 20 L batches) at €35.3/L (€706).<sup>39</sup> The case also illustrates the need for successful partnerships with the raw biomaterial suppliers, through which the bioeconomy company can access large volumes of low-value biomass, ideally coming out of an existing and preferably not distant facility. Indeed the Dutch company advertises online its 'PeelPickup' service explaining to potential suppliers having 'kilos of orange peels lying around after squeezing fresh juice' that they 'will be happy to pick them up from you'.<sup>35</sup> Successful partnership extends also to technology providers. For instance, along with the screw conveyor supplier the company developed a new peel squeezer conveyor that avoids release of pectin due to hard squeezing and that worsens the orange oil extraction and also has a negative effect on the quality of the oil due to emulsion formation.<sup>40</sup>

## Conclusions

The cases of synthetic amorphous silica, pectin, polysaccharide nanofiber, pelargonic acid, hydrogen peroxide from water, dietary fiber and orange oil from fresh orange peel, discussed in this study suggest that three main

requirements, identified in Table 2, need to be met for a successful bioproduction method.

The production of synthetic amorphous silica from rice hull ash was industrialized (between 2016 and 2022)<sup>7-9</sup> when it became clear to chemical industry managers that the raw material (rice hull ash) readily available from nearby rice-processing companies could be converted into SAS at a fraction of the capital and operational expenditure required by the energy-intensive route starting from silica sand and limestone. Remarkably, the bioproduction method *also* started at a company that has been using the conventional technology for over a century (and continues to use it).<sup>7</sup>

In the case of pectin, what is required for new biobased production methods competing with the incumbent technology is substantially lower capital and operating expenditure. The latter, in turn, requires the use of (i) water only no chemicals or organic solvent during extraction or isolation, and (ii) a drastic reduction in the amount of energy in comparison with both extraction and isolation steps of the conventional production route.

Extraction from different citrus fruit peels using steam flash hydrolysis (in acidic water),<sup>41</sup> microwaves,<sup>42</sup> and cavitation<sup>43-45</sup> bubbles in water only has been demonstrated on a semi-industrial scale. It is therefore not surprising to learn that new plants using similar technologies have recently started to operate. For example, one company has recently built, in Israel, the first modular pectin production plant based on acoustic cavitation-assisted extraction. The company will produce 1000 t/year of pectin and 3000 t/year of dietary fiber (3 t of pectin and 8-9 t of dietary fiber per day).<sup>46</sup>

In the case of pelargonic acid, this fatty acid will become the active ingredient of new-generation herbicides chosen by farmers and gardeners, as well as for eliminating annual and perennial weeds in urban and industrial areas, when its price and accessibility will become comparable with those of existing synthetic products generally obtained from petroleum feedstocks by the chemical industry. Herbicides based on nonanoic acid are also biodegradable rapidly in the soil and, with very low water solubility, do not generate residues in the soil or on treated plants, and thus do not affect the germination of seeds in the soil or root systems, leaving the fertility of the soil unaltered and preserving its biodiversity and resistance to erosion.

Seen from this wider perspective, the conflicting dynamics intrinsic to the transition to the bioeconomy should become more evident to bioeconomy and green chemistry practitioners. The conflict here is not that between environmental and economic goals on how to allocate biological resources (i.e., biomass and soil) between different industries and uses (typically to make heavily incentivized

biofuels),<sup>47</sup> but that between existing and new manufacturers of valued chemical products.

By studying, for example, the case of bioplastics, both bioeconomy managers and green chemistry researchers will learn that, like in the case of the ‘sailing ship effect’ 150 years ago, during which, after the steamboats appeared, ‘a sudden increase of innovation activities in the incumbent sailing technology was observed with the intention to prevent the fast entry of, and replacement by, steamboats’,<sup>48</sup> the chemical industry adopted a cooperation strategy to internalize the new knowledge, and enlarge their product portfolio. The ‘appearance of potential competitors introducing bio-based solutions’, wrote Pyka and co-workers ‘triggered innovation in the established fossil-based industry with a motivation to prolong their dominance in the market.’<sup>48</sup>

In other words, bioeconomy managers need to receive updated education, including education in fundamental aspects of science and technology concerning their broad field of activity.<sup>49</sup> The education of green chemistry researchers needs to be expanded to include economic and management aspects that cannot be ignored any longer. Like the chemical and energy industries, the bioeconomy has an intrinsic global nature. Hence, this study will hopefully be used as an additional resource for such expanded learning and educational activities across the world.

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## Conflict of interest

The authors declare no conflict of interest.

## References

1. Anastas PT and Williamson TC (eds), *Green Chemistry: Designing Chemistry for the Environment*, Vol. 626. ACS Symposium Series, American Chemical Society, Washington, DC (1996).
2. Linthorst JA, An overview: Origins and development of green chemistry. *Found Chem* 12:55–68 (2010). <https://doi.org/10.1007/s10698-009-9079-4>.
3. Staffas L, Gustavsson M and McCormick K, Strategies and policies for the bioeconomy and bio-based economy: An analysis of official national approaches. *Sustainability* 5:2751–2769 (2013). <https://doi.org/10.3390/su5062751>.
4. Pagliaro M, The central role of chemistry in the transition to the solar economy: The outcomes of two lectures at the Russian Academy of Sciences. *Gen Chem* 6:200007 (2020). <https://doi.org/10.21127/yaoyigc20>.
5. Befort N, From the development of industrial chemistry to the emergence of the bioeconomy, in *The Bioeconomy*, ed. by Befort N. Routledge, London (2023). <https://doi.org/10.4324/9781003103011-3>.
6. Pagliaro M, An industry in transition: The chemical industry and the megatrends driving its forthcoming transformation. *Angew Chem Int Ed* 58:11154–11159 (2019). <https://doi.org/10.1002/anie.201905032>.
7. Solvay, Bio-Circular Silica for Eco-Friendlier Tires (2023). Available: <https://www.solvay.com/en/article/reducing-carbon-footprint-tires> [9 November 2023].
8. Evonik in tie-up with Austria/Thailand for biobased silica. *Rubber Journal Asia*, (2022). Available: <https://rubberjournalasia.com/evonik-in-tie-up-with-austria-thailand-for-biobased-silica/> [9 November 2023].
9. Yadav JNK, Paul M, Singh H, Singh A, Kundu S, Kumar Y et al., Composition, application and recycling of RHA to value-added products: A review. *J Pharm Negat Results* 14:3772–3787 (2023). <https://doi.org/10.47750/pnr.2023.14.03.473>.
10. Kalapathy U, Proctor A and Shultz J, A simple method for production of pure silica from rice hull ash. *Bioresour Technol* 73:257–262 (2000). [https://doi.org/10.1016/S0960-8524\(99\)00127-3](https://doi.org/10.1016/S0960-8524(99)00127-3).
11. Pörner Ingenieurgesellschaft, *Bio-Silicate Technology*, (2022). Available: [https://www.poerner.at/fileadmin/user\\_upload/POE\\_Flyer\\_Bio-Silicates\\_2022\\_E\\_Web.pdf](https://www.poerner.at/fileadmin/user_upload/POE_Flyer_Bio-Silicates_2022_E_Web.pdf) [9 November 2023].
12. Pörner operates a semi-industrial pilot plant in Germany, where the company tests rice hull ashes from different rice plants to check if they are suitable for silicate production and produce trial quantities for industrial applicants. Pörner Gruppe, Process Plants by Pörner (2022). Available: [https://www.biturox.com/fileadmin/user\\_upload/POE\\_Imagebrosc huere\\_2022\\_E\\_web.pdf](https://www.biturox.com/fileadmin/user_upload/POE_Imagebrosc huere_2022_E_web.pdf) [9 November 2023].
13. Seisun D and Zalesny N, Strides in food texture and hydrocolloids. *Food Hydrocoll* 117:106575 (2021). <https://doi.org/10.1016/j.foodhyd.2020.106575>.
14. Chan SY, Choo WS, Young DJ and Loh XJ, Pectin as a rheology modifier: Origin, structure, commercial production and rheology. *Carbohydr Polym* 161:118–139 (2017). <https://doi.org/10.1016/j.carbpol.2016.12.033>.
15. Adetunji LR, Adekunle A, Orsat V and Raghavan V, Advances in the pectin production process using novel extraction techniques: A review. *Food Hydrocoll* 62:239–250 (2017). <https://doi.org/10.1016/j.foodhyd.2016.08.015>.
16. Muhidinov ZK, Ikromi KI, Jonmurodov AS, Nasriddinov AS, Usmanova SR, Bobokalonov JT et al., Structural characterization of pectin obtained by different purification methods. *Int J Biol Macromol* 183:2227–2237 (2021). <https://doi.org/10.1016/j.ijbiomac.2021.05.094>.
17. Qi Y, Guo Y, Liza AA, Yang G, Sipponen MH, Guo J et al., Nanocellulose: A review on preparation routes and applications in functional materials. *Cellulose* 30:4115–4147 (2023). <https://doi.org/10.1007/s10570-023-05169-w>.

18. Ciriminna R, Ghahremani M, Karimi B and Pagliaro M, Emerging green routes to nanocellulose. *Biofuels Bioprod Biorefin* **17**:10–17 (2023). <https://doi.org/10.1002/bbb.2423>.
19. Jun SH, Park SG and Kang NG, One-pot method of synthesizing TEMPO-oxidized bacterial cellulose nanofibers using immobilized TEMPO for skincare applications. *Polymers* **11**:10 (2019). <https://doi.org/10.3390/polym11061044>.
20. Patankar SC and Renneckar S, Greener synthesis of nanofibrillated cellulose using magnetically separable TEMPO nanocatalyst. *Green Chem* **19**:4792–4797 (2017). <https://doi.org/10.1039/c7gc02383a>.
21. Tsao Y-H and Chen L-C, *Development and Characterization of SiliaCat TEMPO-Oxidized Sacchachitin, 2021 across the Taiwan Strait and International Student Academic Conference, Taiwan*, (2021). Available <http://repository.unism.ac.id/1779/56/2021%20International%20Students%20Academic%20Conference%281%29.pdf> [8 November 2023].
22. Chao F-C, Wu M-H, Chen L-C, Lin H-L, Liu D-Z, Ho H-O et al., Preparation and characterization of chemically TEMPO-oxidized and mechanically disintegrated sacchachitin nanofibers (SCNF) for enhanced diabetic wound healing. *Carbohydr Polym* **229**:115507 (2020). <https://doi.org/10.1016/j.carbpol.2019.115507>.
23. Ciriminna R, Fidalgo A, Ilharco LM and Pagliaro M, Herbicides based on pelargonic acid: Herbicides of the bioeconomy. *Biofuels Bioprod Biorefin* **13**:1476–1482 (2019). <https://doi.org/10.1002/bbb.2046>.
24. Bastioli C, Milizia T and Borsotti G, Improved process for the production of derivatives of saturated carboxylic acid, EP1926699B1 (2005).
25. Godard A, De Caro P, Vedrenne E, Mouloungui Z and Thiebaut-Roux S, From crops to products for crops: Preserving the ecosystem through the use of bio-based molecules. *OCL* **23**(5):D510 (2016). <https://doi.org/10.1051/oc/2016037>.
26. Bastioli C, Borsotti G, Merlin A and Milizia T, Process for the catalytic cleavage of vegetable oils, US8222438B2 (2012).
27. Matrica M, *Porto Torres Inaugurates New Green Chemistry Complex*, (2014). Available: <https://www.matrica.it/article.asp?id=37&ver=en> [8 November 2023].
28. Novamont, FIRST2RUN – Flagship demonstration of an integrated biorefinery for dry crops sustainable exploitation towards biobased materials production, Ref. Ares (2016) 3165310 (2016). Available: <https://ec.europa.eu/research/participants/documents/downloadPublic?documentIds=080166e5aa9dc1b4&appId=PPGMS> [8 November 2023].
29. HPNow, Products, Copenhagen (2023). Available: <https://www.hpnow.eu/on-site-hydrogen-peroxide-products/> [9 November 2023].
30. Siahrostami S, Verdaguer-Casadevall A, Karamad M, Deiana D, Malacrida P, Wickman B et al., Enabling direct H<sub>2</sub>O<sub>2</sub> production through rational electrocatalyst design. *Nature Mater* **12**:1137–1143 (2013). <https://doi.org/10.1038/nmat3795>.
31. Agrosources Irrigation, *HPNow A Series-on-Site Generation of Hydrogen Peroxide*. Santa Maria, CA (2023). Available: <https://agrosourcesgroup.com/product/hpnow-on-site-generation-of-hydrogen-peroxide-3/> [11 December 2023].
32. EIFO, *EIFO and Novo Holdings Lead €14M Round in Power-to-Peroxide Pioneer HPNow*. Copenhagen (2023). Available: <https://eifo.dk/en/knowledge/news/eifo-and-novo-holdings-lead-14m-round-in-power-to-peroxide-pioneer-hpnow/> [9 November 2023].
33. Almena A and Martín M, Technoeconomic analysis of the production of epichlorohydrin from glycerol. *Ind Eng Chem Res* **55**:3226–3238 (2016). <https://doi.org/10.1021/acs.iecr.5b02555>.
34. KVT to Build Epichlorohydrin Production Complex in China, CHEManager (2021). Available: <https://www.chemanager-online.com/en/news/kvt-build-epichlorohydrin-production-complex-china> [8 November 2023].
35. PeelPioneers BV, Den Bosch, the Netherlands (2023). Available: <https://peelpioneers.nl> [7 December 2023].
36. Dai H, Chen Y, Ma L, Zhang Y and Cui B, Direct regeneration of hydrogels based on lemon peel and its isolated microcrystalline cellulose: Characterization and application for methylene blue adsorption. *Int J Biol Macromol* **191**:129–138 (2021). <https://doi.org/10.1016/j.jbiomac.2021.09.063>.
37. Siles López JÁ, Li Q and Thompson IP, Biorefinery of waste orange peel. *Crit Rev Biotechnol* **30**:63–69 (2010). <https://doi.org/10.3109/07388550903425201>.
38. Neves MF, Trombin VG, Marques VN and Martinez LF, Global orange juice market: A 16-year summary and opportunities for creating value. *Trop Plant Pathol* **45**:166–174 (2020). <https://doi.org/10.1007/s40858-020-00378-1>.
39. See at: 1-2-Taste, PeelPioneers – Cold Pressed Oil Natural Orange (2023). Available: <https://www.12taste.com/it/product/peelpioneers-orange-cold-pressed-oil/> [7 December 2023].
40. van Beek, Collaborative R&D project between Van Beek and PeelPioneers results in revolutionary Soft Squeezer, Drunen (the Netherlands) (2022). Available: <https://www.van-beek.nl/en/collaborative-rd-project-between-van-beek-and-peelpioneers-results-in-revolutionary-soft-squeezer/> [7 December 2023].
41. Muhidinov Z, Teshaev K, Jonmurodov A, Khalikov D and Fishman M, Physico-chemical characterization of pectic polysaccharides from various sources obtained by steam assisted flash extraction (SAFE). *Macromol Symp* **317–318**:142–148 (2012). <https://doi.org/10.1002/masy.201100108>.
42. Ciriminna R, Fidalgo A, Carnaroglio D, Cravotto G, Grillo G, Tamburino A et al., Eco-friendly extraction of pectin and essential oils from orange and lemon peels. *ACS Sust Chem Eng* **4**:2243–2251 (2016). <https://doi.org/10.1021/acssuschemeng.5b01716>.
43. Wang W, Ma X, Xu Y, Cao Y, Jiang Z, Ding T, et al., Ultrasound-assisted heating extraction of pectin from grapefruit peel: Optimization and comparison with the conventional method. *Food Chem* **178**:106–114 (2015). <https://doi.org/10.1016/j.foodchem.2015.01.080>.
44. The process has been scaled-up on semi-industrial scale for example by Hielscher Ultrasonics, Higher Pectin Yields with Ultrasonic Extraction (2023). Available: <https://www.hielscher.com/higher-pectin-yields-with-ultrasonic-extraction.htm> [9 November 2023].
45. Meneguzzo F, Brunetti C, Fidalgo A, Ciriminna R, Delisi R, Albanese L et al., Real-scale integral valorization of waste orange peel via hydrodynamic cavitation. *Processes* **7**:581 (2019). <https://doi.org/10.3390/pr7090581>.
46. Batushansky B, Personal Information to M.P (2023). Available: <https://pulvit.com> [9 November 2023].
47. McCormick K, The bioeconomy and beyond: Visions and strategies. *Biofuels* **5**:191–193 (2014). <https://doi.org/10.1080/17597269.2014.913882>.
48. Pyka A, Ari E, Alva-Ferrari A and Urmetzer S, The bioeconomy transition process: Sailing through storms and doldrums in unknown waters. *J Innov Econ Manag* **38**:35–61 (2022). <https://doi.org/10.3917/jie.pr.1.0110>.
49. Ciriminna R, Albanese L, Meneguzzo F and Pagliaro M, Educating the managers of the bioeconomy. *J Clean Prod* **366**:132851 (2022). <https://doi.org/10.1016/j.jclepro.2022.132851>.

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