

# Biobased Silicon and Biobased Silica: Two Production Routes Whose Time has Come\*\*

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This study offers an updated bioeconomy perspective on biobased routes to high-purity silicon and silica in the context of the societal, economic and environmental trends reshaping chemical processes. We summarize the main aspects of the green chemistry technologies capable of transforming current

production methods. Coincidentally, we discuss selected industrial and economic aspects. Finally, we offer perspectives of how said technologies could/will reshape current chemical and energy production.

## 1. Introduction

Silicon, found mostly as silica (SiO<sub>2</sub>) or silicates (e.g. Si<sub>2</sub>O<sub>3</sub><sup>2-</sup>) comprising more than 40% of the earth's crust serve as primary sources for several multibillion dollar industries including the silicone polymers, photovoltaics, and electronics (semiconductors). The use of SiO<sub>2</sub> as a chemical raw material has relied, to date, exclusively on the equipment-, capital- and energy-intensive carbothermal reduction of quartz carried out at 1900 °C in arc furnaces affording metallurgical grade silicon (Si<sub>MG</sub>, ca. 98% purity).<sup>[1]</sup> The process requires around 10–11 kWh to produce one kilogram of Si<sub>MG</sub><sup>[2]</sup> with electricity accounting for 40% of the total production cost.<sup>[3]</sup>

In 2022 more than 3 million tons of Si<sub>MG</sub> were produced while demand was substantially higher (3.5–3.75 million tons) leading to 300% price increases to \$6000–9000 per ton from \$2000–3000 per ton in 2021.<sup>[3]</sup> Alone, China in 2020–21 accounted for ~80% of the 3 million tons per year annual production, followed by Europe and the Americas. Nearly half (~45%) of the total demand originates from aluminum alloys, ~35% from silicones, ~15% from photovoltaic cells, and ~5% from the semiconductor industry.<sup>[3]</sup> Driven by increasing demand for silicon from the solar photovoltaic industry, the market for Si<sub>PV</sub> has nearly doubled since 2010.<sup>[4]</sup> The industry

continues to expand capacity with an expected increase in production capacity between 0.5 and 1 million tons per year between 2023 and 2025.<sup>[3]</sup> Due to reduced cost of production (lowering cost of electricity), by early 2023 prices dropped by 60%, averaging at \$2000–3000 per ton.<sup>[3]</sup>

The aluminum and silicones industries use Si<sub>MG</sub> directly for alloys and production of Me<sub>x</sub>SiCl<sub>4-x</sub> (Si<sub>MG</sub> is reacted with methyl chloride, the Rochow–Muller process). The photovoltaic and semiconductor industries require “solar-grade” and “electronics-grade” silicon of exceptionally high purity (99.999%, 5N, to 99.9999999%, 9N). In more detail, powdered Si<sub>MG</sub> is reacted with anhydrous HCl at 300 °C in a fluidized bed reactor to form both SiCl<sub>4</sub> and SiHCl<sub>3</sub>. The latter silane is further reacted with hydrogen at 1100 °C for ~200–300 h. The reaction takes place inside large vacuum chambers and the silicon is deposited onto thin polysilicon rods (small grain size silicon) to produce high-purity polysilicon rods of diameter 150–200 mm.<sup>[5]</sup>

The aforementioned (“Siemens”) process was developed in Germany in the 1960s to produce electronic-grade silicon and is still used to, to manufacture all high purity Si needed for the semiconductor and PV industries.

The polysilicon industry has made dramatic advances in terms of expanding capacity and lowering production costs chiefly in China. Starting from almost zero in 2004, in 2021 it accounted for more than 75% of the global polysilicon output, with demand for solar-grade polysilicon reaching ca. 465,000 t in 2017.<sup>[6]</sup> As a result, in 2019, the polysilicon spot price fell below the historical mark of \$9/kg and closed the year at \$8.50 per kg.<sup>[7]</sup> For comparison, in 2008 when the global solar PV boom started to unfold<sup>[8]</sup> the price was \$360 per kg.<sup>[7]</sup> Today (mid 2023), the price stands at about \$20 per kg, and capacity is still expanding.

However, the need for a new technology to manufacture high purity silicon using new chemical technologies of dramatically lower capital and energy intensity remains a global challenge of great economic, societal and environmental relevance. For example, the investment cost for a conventional Siemens-type plant of 1000 tons per year in 2010 was around 100 million €<sup>[9]</sup> and has since increased considerably. Furthermore, the engineering, construction and ramp-up of a new polysilicon plant can easily take three years, intrinsically causing

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supplies to lag behind demand as demand rises, thus driving price volatility.<sup>[6]</sup>

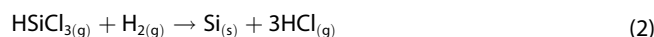
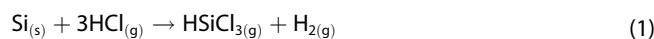
The technology, we argue in this study, exists and is based on the direct conversion of bioderived SiO<sub>2</sub> containing rice hull ash (RHA) to solar-grade silicon.<sup>[10]</sup> Similarly, the energy-, capital-, and equipment-intensive technology to produce valued synthetic amorphous precipitated silica (SAS) that currently uses stoichiometric base depolymerization of SiO<sub>2</sub> to form either sodium (or potassium) silicate<sup>[11]</sup> followed by reaction with stoichiometric H<sub>2</sub>SO<sub>4</sub> must be replaced by a more environmentally acceptable process. For example, it is now possible to depolymerize silica using catalytic base in the presence of alcohols especially diols such as ethylene glycol or hexylene glycol to afford in the later case distillable alkoxy-silanes (e.g. spiro-siloxanes, SP) in one-pot at low temperature.<sup>[12–14]</sup> Currently obtained by reacting SiCl<sub>4</sub> with alcohols, tetraalkoxysilanes such as tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) are key precursors to silica-based sol-gel materials. Their direct synthesis at lower cost from biobased silica or replacement with SP would open-up sol-gel applications that remained elusive (e.g. aerogels) due to the high cost of said precursors.<sup>[15]</sup>

Comprised of ~85% amorphous silica, RHA is a highly reactive pozzolanic byproduct from combustion of rice protective outer shells (hulls) to generate electricity following rice milling. The material is currently sold to the steel industry (where the ash is placed on top of ladles of molten steel to retain heat), as well as an adsorbent for water filtration, and as an additive to promote retention of water and fertilizer in soils.<sup>[16]</sup> In the following, we offer an updated bioeconomy perspective on a biobased route to high-purity silicon and silica in the context of the societal, economic and environmental megatrends driving the reshaping of chemical productions.<sup>[17]</sup> First, we summarize the main aspects of the green chemistry technologies. Thereafter, we discuss selected industrial and economic aspects. Finally, we present our personal insight into the perspective of said technologies put in context of the aforementioned reshaping of chemical<sup>[17]</sup> and energy<sup>[8]</sup> productions.

## 2. Green Chemistry Technologies

### 2.1. Production of biobased silicon

As mentioned in the introduction, the polysilicon industry in China, starting from almost zero in 2004, in 2021 already accounted for more than 75% of the global polysilicon output, with demand for solar-grade polysilicon reaching ca. 465,000 t in 2017.<sup>[6]</sup> Most (90%) polysilicon plants today use the Siemens process in which metallurgical-grade silicon is first hydrochlorinated to form trichlorosilane (and SiCl<sub>4</sub> which is burned in H<sub>2</sub>/O<sub>2</sub> to form fumed silica while HCl is recycled) at 300 °C and 1 bar (Eq. (1)), and then the latter diluted with high-purity hydrogen at 1100 °C is decomposed (Eq. (2)) forming pure polycrystalline silicon along with gaseous HCl (recovered and reused):<sup>[18]</sup>



Both processes (the Siemens process and the Union Carbide process) are employed for the industrial production of solar-grade silicon. However, both are atomically inefficient as they respectively afford 11–14 and 22–27 tons of unwanted SiCl<sub>4</sub> per ton of solar-grade Si through the disproportionation of trichlorosilane (Eq. (3)).<sup>[19]</sup>

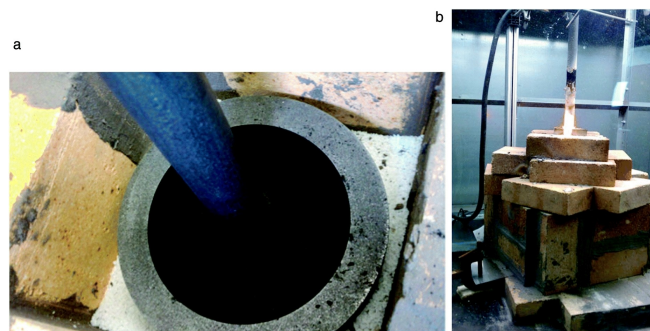


In the biobased process, production of solar-grade silicon, the carbon present in RHA is used to promote the conversion of SiO<sub>2</sub> in RHA to ultrapure silicon in a surprisingly simple process involving a facile RHA purification step using only dilute acid and hot water followed by addition of a small amount of highly pure graphite and finally by carbothermal reduction using a small 50 kW electric arc furnace operated at 1700–2100 °C in batch mode (Figure 1).<sup>[10]</sup>

In greater detail, RHA is purified at low temperature by first milling the RHA in dilute (3.7 wt%) HCl, filtering and then washing with cold and then boiling water at up to 10 kg (initial weight) quantities. At industrial scales, the energy required to purify RHA is estimated by the team at 5 kWh kg<sup>-1</sup> for solar-grade Si (Si<sub>PV</sub>) produced.

This quantity is ≈5× less than the electricity needed for traditional processing of Si<sub>PV</sub> (23 kWh kg<sup>-1</sup>). One can easily envision this energy coming from combustion of RHs with coincident collection of RHA.

Prior to carbothermal reduction, the purified RHA kept in pH neutral distilled water in a 30 L polyethylene container was treated with ammonium hydroxide to obtain a pH 8 suspension, filtered and the wet cakes shaped into 30 g spherical pellets containing a small amount of high purity (electronics grade) graphite. After, air drying at 230 °C for 24 h, the pellets were carbothermally reduced to obtain Si<sub>PV</sub>. Typical processing involved adding 3.6 kg of pellets to the arc furnace followed by introduction of an additional 3.6 kg charge every 6 h after the start of carbothermal reduction. Purities were found to be



**Figure 1.** Interior of the electric arc furnace with 1/3 of the feedstock loaded (left). The furnace in operation (right), 50×50×100 cm [Reproduced from Ref. [10], Copyright (2015) with kind permission from RSC Publishing].

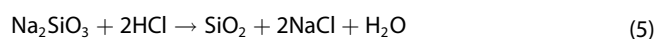
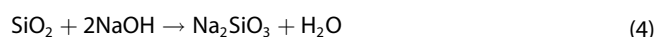
99.9999 wt% (6Ns) with B contents of  $\approx 0.1$  ppm by weight. Remarkably, even using this experimental arc furnace at pre-pilot scales, the purities were reproducible:  $\text{Si}_{\text{PV}}$  was consistently obtained in subsequent experiments (“production campaigns” to use the jargon of the fine chemical industry).

The small reactor size does not allow  $\text{SiO}_{(\text{g})}$  intermediate in  $\text{SiO}_2$  reduction to condense back into the reactor as in industrial reactors, more than 50% of the added biobased silica is lost as  $\text{SiO}_{(\text{g})}$ . The highest yields were obtained by partially filling the reactor with the feedstock, and then adding the rest in several increments. The resulting high concentration of  $\text{SiO}_{(\text{g})}$  in the reactor results in partial condensation back into the reaction zone. In this way, it was possible to reach a  $37 \pm 5\%$  theoretical yield of  $\text{Si}_{\text{PV}}$  (1.6 kg per batch), which is a surprisingly high yield for an experimental electric arc furnace reactor.

Finally, the submicron (nanometer scale) intimate mixing of carbon and  $\text{SiO}_2$  naturally present in the RHA feedstock results in much smaller diffusion distances during carbothermal reduction when compared to those in quartz/coal feedstock. Accordingly, and unprecedented; a quite fast reaction rate was observed, roughly 4x faster than the rate of quartz/coal feedstock conversion in  $\text{Si}_{\text{MG}}$ . This suggests that high throughput  $\text{Si}_{\text{PV}}$  can be obtained using a continuous reactor or a smaller arc furnace further reducing the amount of electricity needed to produce the same amounts of  $\text{Si}_{\text{PV}}$  using RHA in place of a quartz/coal feedstock.<sup>[10]</sup>

## 2.2. Production of biobased silica

Silica in RHA can be efficiently converted into pure sodium silicate solution, and thus to ultrapure silica following precipitation with acid. The reactions (Eqs. (4) and (5)) are simple and effective; however, there is still a simpler way as we show below.



The process was demonstrated in 2000 obtaining ultrapure silica<sup>[20]</sup> whereas the technology was developed by an Austrian company operating a demonstration plant in Germany since 2016.<sup>[21]</sup> Basically, the company reacts RHA with aqueous NaOH (or with more expensive KOH if potassium silicate is desired) heating the reaction mixture in a first reactor to greater than 90 °C at a pressure  $\geq 1$  bar forming a sodium silicate solution with soluble contaminants and undissolved nanoporous carbon particles, which are removed by filtration. After filtering, the silicate solution is concentrated to meet customer specifications.<sup>[21]</sup>

In 2016 Laine and co-workers reported the first version of the direct route from biobased  $\text{SiO}_2$  contained in RHA to TEOS/TMOS and distillable spirocyclic alkoxysilanes relying on the base-catalyzed depolymerization of  $\text{SiO}_2$  with diols.<sup>[14]</sup> In detail, in a scaled experiment, a mixture of 630 g of acid purified RHA (specific surface area,  $\text{SSA} \approx 85 \text{ m}^2 \text{ g}^{-1}$ , 7.87 mol  $\text{SiO}_2$ ) with a

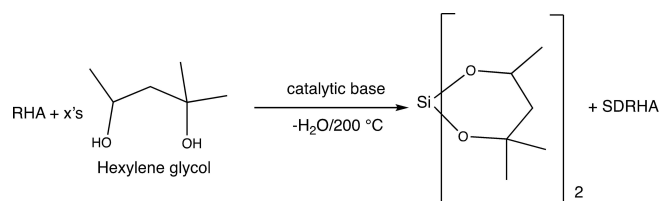
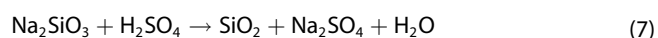
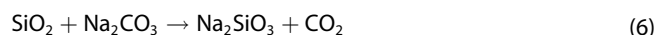
silica content of 75 wt% was reacted at 200 °C with NaOH (10 mol%) and ethylene glycol (EGH<sub>2</sub>, 7 L) for 20 h distilling away  $\text{H}_2\text{O}$  to drive the reaction. The glycol reacts with the silica to form tetraglycoxysilane  $\text{Si}(\text{EGH}_2)_4$  with good conversion. RHA's high  $\text{SSA} \approx 80 \text{ m}^2 \text{ g}^{-1}$ , and poor crystallinity substantially accelerate the reaction. This compound, although resulting from direct depolymerization of RHA's silica, is not distillable and can only be heated to form a polymeric material  $\text{Si}(\text{eg})_2$  which can be acidified with HCl in the presence of EtOH to give TEOS, but the yields are poor.

Recent efforts by the Laine's group have solved a number of problems noted above especially with the ethylene glycol studies. If one substitutes the hindered diol (e.g. hexylene glycol) for ethylene glycol then it is possible to form spiroloxanes as illustrated in Scheme 1.

The spiroloxane (SP) distills directly out the reaction mixture and can be easily recovered from unreacted diol by washing with hexane and then water to dissolve the diol but not SP.

In the above reaction that starts with ethylene glycol depolymerization, one can switch, after 24 h and  $\sim 37\%$  silica dissolution, to synthesize the spiroloxane  $\text{Si}(2\text{-methyl-2,4-pentanediolato})_2$  (SP) by adding 3.5 L of hexylene glycol (2-methyl-2,4-pentanediol). SP distillation readily starts and SP distills out ( $\sim 3$  L) and is collected. Straightforward work up [addition of hexane (3 L) and water ( $3 \times 1$  L) washing steps] affords highly pure SP which can be thereafter be combusted or treated with water and trace acid to afford high-purity fumed or precipitated silica.

The process thereby replaces the conventional process for making precipitated silica in which silica sand is reacted with sodium carbonate at 1300 °C to form sodium silicate glass, which is then dissolved in water and amorphous silica is precipitated out by adding one equivalent of sulfuric acid affording one sodium sulfate and one  $\text{CO}_2$  per ton  $\text{SiO}_2$  (Eqs. (6) and (7)). Alternately, the SP can be combusted to produce fumed silica in a  $\text{H}_2/\text{O}_2$  flame, escaping the need for  $\text{SiCl}_4$  (Eq. (8)).



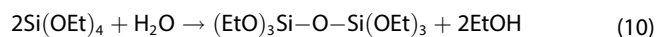
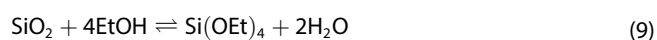
**Scheme 1.** Direct distillative removal of silica with coincident production of silica-depleted rice hull, SDRHA 40–70 (40–70 wt% remaining silica; x's stands for “excess”).

Because it is possible to adjust the silica content of the remaining silica-depleted RHA (SDRHA) it is possible now to control the  $\text{SiO}_2\text{:C}$  ratio which in principle means that if one were to make solar-grade Si from this SDRHA no additional carbon needs be added. The material is ready for direct carbothermal reduction to produce silicon metal with 99.9999% purity without further purification.<sup>[10]</sup>

It was further demonstrated that SDRHA can be used simply as is to make SiC,  $\text{Si}_3\text{N}_4$  or  $\text{Si}_2\text{N}_2\text{O}$  on heating at 1400–1500 °C in Ar,  $\text{N}_2$  or  $\text{N}_2\text{:H}_2$  (85:15) in high yield and at 400–500 °C below traditional synthesis temperatures again because of SDRHA's nanocomposite nature.<sup>[22]</sup> Still another advantage comes from controlling the  $\text{SiO}_2\text{:C}$  ratio, as it is possible to coincidentally produce small amounts of hard carbon (HC) with the SiC,  $\text{Si}_2\text{N}_2\text{O}$ . HC is a mixture of graphitic and amorphous carbon. HC is quite advantageous in improving the behavior of lithium ion batteries.<sup>[23,24]</sup>

Finally, the SiC/HC ( $\text{Si}_2\text{N}_2\text{O}$ /HC) mixtures produced from SDRHA can serve as anodes in lithium ion batteries offering capacities of  $\sim 950$  (750)  $\text{mAhg}^{-1}$  which is three times that of traditional graphite anodes in lithium ion batteries.<sup>[25]</sup> Additionally, these systems undergo a volume change of  $\leq 1\%$  potentially making them competitive with silicon-based lithium ion batteries.<sup>[25]</sup> Note that most high purity graphite used in Li-ion batteries commercially produced today is synthetic and produced at  $\sim 2000$  °C making it a  $\text{CO}_2$ , energy and equipment intensive process. The HC produced coincident with SiC is pure enough to at least in part supplant the need for graphite in these systems again, indicating an economic and green reward derived from RHA.

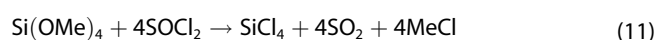
In 2017, Fukaya and co-workers reported the synthesis of TEOS in 75% yield by simply reacting RHA-derived silica (15 mmol), with 10 mol% KOH catalyst, and 100 mL of EtOH at 240 °C for 6 h in a 200 mL autoclave, using 25 g of 3 Å molecular sieves.<sup>[12]</sup> Key to shifting the equilibrium reaction in Eq. (9) is the presence in an upper autoclave of the molecular sieves promoting the reaction between silica and ethanol by adsorbing water molecules vaporized from the reaction mixture (without dehydrating agent, the TEOS yield is only 4%),<sup>[26]</sup> minimizing formation of hexaethoxydisiloxane (Eq. (10)):



Further lowering the process cost, a simple treatment under vacuum at 300 °C regenerates the spent molecular sieves.<sup>[12]</sup> Three years later, the team extended this approach based on water removal by using 2,2-dimethoxypropane as a dehydrant under carbon dioxide in the synthesis of tetramethoxysilane.<sup>[13]</sup> The synthesis of TMOS starts directly from silica obtained from renewable biomass such as rice hull ash, straw, pampass grass or bamboo, and employs only methanol, and dimethyl acetals with a base catalyst under  $\text{CO}_2$  at 240 °C. For example, starting from RHA with 2,2-dimethoxypropane at 240 °C for 24 h under 0.8 MPa  $\text{CO}_2$  on a 1 L-scale reaction, TMOS was obtained in 69% yield.

Research continued, and the Japan-based team eventually reported that the use of cheap and readily available CaO as dehydrating agent further enhances the economic viability of the process.<sup>[26]</sup>

Together, the biobased routes to high-purity Si,  $\text{SiO}_2$  and  $\text{Si}(\text{OR})_4$  entirely by-pass the need for  $\text{Si}_{\text{MG}}$  derived by the carbothermal reduction of quartz, establishing a circular bioeconomic route to all the primary silicon compounds employed in the chemical industry. Indeed, also chloromethane, a key raw material for the silicone industry, reacted with elemental silicon in the Rochow-Müller "direct process" to form methylchlorosilanes, can be readily synthesized from alkoxy-silanes TEOS or TMOS.<sup>[27]</sup> For instance, TMOS can be quantitatively converted into  $\text{SiCl}_4$  and MeCl (Eq. (11)) by reaction with four equivalents of  $\text{SOCl}_2$  at 90 °C under a  $\text{N}_2$  in the presence of a catalytic amount of tetrabutylammonium chloride (TBAC, 0.4 equiv.):



Thionyl chloride is a versatile reagent widely used by the chemical industry for the synthesis of carboxylic acid chlorides, with many advantages compared with other chlorinating reagents, including ease of isolation of  $\text{SO}_2$  end product, ease of handling (miscible with nearly all organic solvents), and very high yield in chlorinated products.<sup>[28]</sup> However, for commodity chemical production as is the case here, it is unlikely to be adopted for commercial scale levels of production.

What are thus the main obstacles to industrial uptake of these bioeconomy technologies introduced in certain cases more than twenty years ago? What, if any, has changed in the chemical and energy production contexts, that now supports their commercialization and industrial uptake?

### 3. Economic and Industrial Aspects

With yearly installations having crossed in 2022 the 240 GW threshold and production of solar cells and wafers in the 300 GW range,<sup>[29]</sup> the solar photovoltaic (PV) technology already plays a crucially important role in the global energy generation mix. In 2022, the overall 1 TW power of PV systems installed worldwide generated over 1000 TWh, which already approaches 4% of the total electricity produced in 2020 (26823 TWh).<sup>[30]</sup>

Under these circumstances, it is now clear that manufacturing polysilicon is a crucial requirement for national energy security for all major economies. This is true both for economically developed countries, where solar-grade Si manufacturing existed and was abandoned to be replaced by solar cell and module imports from South East Asia,<sup>[31,32]</sup> and for emerging economies with large populations willing to start to operate their own solar PV and electronic industries such as India, Brazil, South Africa, Turkey, Iran, Pakistan, Indonesia, the Philippines and so on.

Similar arguments hold true for strategically important fine chemical and pharmaceutical productions outsourced to South East Asian countries that after the COVID-19 health crisis are

being urgently reshored to European and North American countries.<sup>[33]</sup> When re-building lost manufacturing capacity, the fine chemical industry will employ new fine chemical manufacturing technologies chiefly based on heterogeneously catalyzed processes carried out under flow in digitally controlled processes using biological raw materials.<sup>[34]</sup> In this case, in fact, production reproducibly takes place with minimal or no waste occurring coincidentally, requiring a tiny fraction of the space, equipment, labor, energy and economic costs required by processes carried out in solution in multipurpose batch reactors followed by expensive purification steps.

In general, Spirosiloxane, TEOS and TMOS obtained from biobased silica can be further converted to useful silicon-based chemicals including chlorosilanes.<sup>[35]</sup>

The biobased production of ultrapure silica and of high-purity silicon starting from RHA rather than from quartz or sand silica discussed in this study are additional examples of this global shift in chemical production driven by megatrends concerning the environment, health, and energy which permeate society on a global scale.<sup>[17]</sup> By escaping the need to produce metallurgical grade silicon as well as of highly toxic chlorosilanes and related gaseous reduction processes currently used in polysilicon production, the new routes can dramatically lower CAPEX (capital expenditures) and OPEX (operational expenditures).

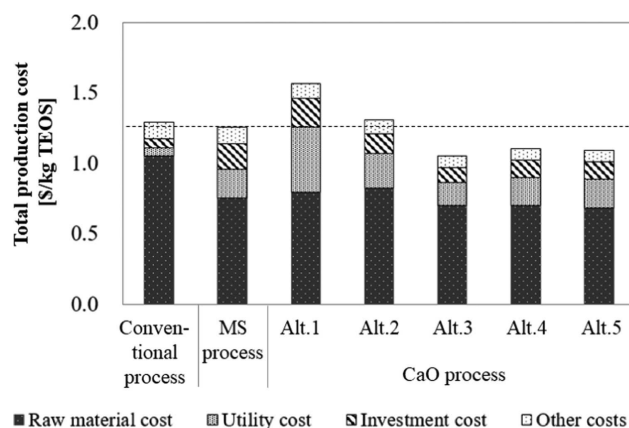
This intrinsically enables the emergence of numerous new manufacturers of both synthetic amorphous silica as well as of solar-grade polysilicon using the aforementioned lean and green chemical processes starting from an overly abundant rice by-product such as the ash produced by rice hull combustion. Perhaps, the only process relying on chlorosilanes for the production of ultrapure silicon will be that of electronic-grade silicon relying on the reduction of  $\text{HSiCl}_3$ .

Fukaya and co-workers adopted a commercial chemical process simulator (for the synthesis process design) based on experimental results to identify optimal TEOS synthesis conditions for selected dehydrating agents minimizing production cost for the simulated production of 1000 tons per year of TEOS with 99.5 wt% purity. Compared to conventional TEOS production from  $\text{Si}_{\text{MG}}$ , the process using CaO for in situ water removal with the optimal  $\text{CaO}/\text{SiO}_2 = 3:1$  molar ratio has a 24% lower cost<sup>[26]</sup> (Alt.3 in Figure 2).

The team carried out a thorough techno-economic analysis aimed at identifying the optimal process conditions in terms of RHA:ethanol molar ratio and energy consumption for the direct synthesis of TEOS.<sup>[36]</sup> Table 1 shows the optimal conditions for the conventional synthesis of TEOS from  $\text{Si}_{\text{MG}}$  and for the new biobased route starting from RHA bringing the highest returns.

Compared to the conventional process chiefly influenced by the price of  $\text{Si}_{\text{MG}}$  and its pronounced volatility, the main cost driver for the new biobased route is the energy “utility” prices (steam, electricity and heavy fuel oil used for product synthesis, ethanol recovery, and product purification) contributing for about 22% to the total cost of the process.

Accordingly, the new technology becomes highly advantageous over the conventional one when using much cheaper rice hull as raw material which costs on average  $0.03 \text{ \$ kg}^{-1}$  vs.



**Figure 2.** Comparison of economic performance of the alternative CaO-driven TEOS synthetic processes compared to the conventional synthesis from  $\text{Si}_{\text{MG}}$ . MS stands for molecular sieves. [Reproduced from Ref. [26], Copyright (2019) with kind permission from ACS Publishing].

**Table 1.** Optimal reaction conditions for TEOS synthesis from  $\text{Si}_{\text{MG}}$  and rice hull ash [Reproduced from Ref. [36], with kind permission].

Parameter	Conventional route	Biobased route
temperature (K)	453	513
raw material	$\text{Si}_{\text{MG}}$	RHA
RHA/EtOH	1:23	1:57
main by-product	triethoxysilane	hexaethyldisiloxane
RHA conversion (%)	88	77.2
yield of TEOS (%)	74	68
yield of by-product (%)	14	4.6

for  $0.15\text{--}0.1 \text{ \$ kg}^{-1}$  for RHA (for comparison, the cost of  $\text{Si}_{\text{MG}}$  is around  $2 \text{ \$ kg}^{-1}$ ) in a integrated production process in which RHA is directly obtained from rice hull incineration producing electricity and steam. Electricity is fed into the national grid while steam is employed in the TEOS production process.

The estimate of the 24% of cost reduction of the biobased route<sup>[36]</sup> to ultrapure synthetic amorphous silica (SAS), takes into account the overall process cost  $C_{\text{tot}}$  amounting to the sum of the investment ( $C_i$ ) and the operating ( $C_o$ ) costs (Eq. (12)):

$$C_{\text{tot}} = C_i + C_o \quad (12)$$

$C_o$  includes the costs of raw materials and energy “utilities” needed to produce, purify and isolate the product, labor, maintenance, and tax.  $C_i$  includes the costs of all the main processing units involved in the synthesis processes, such as reactors, heaters, heat exchangers, and distillation columns. In the biobased route, it is the latter cost to be dramatically lower than the cost of the investment needed to start producing  $\text{Si}_{\text{MG}}$  using an electric arc furnace running at  $1900^\circ\text{C}$ .

The use of highly-dispersible silica to reinforce tires by (partially) replacing low cost carbon black used in treads and, above all, to lower the rolling resistance of tires is of crucial importance to increase the energy efficiency and range of vehicles, which is especially important for battery electric



vehicles, both passenger BEVs and electric buses,<sup>[37]</sup> both now produced in million units per year and growing at fast pace.

It is this large and rapidly increasing demand, we argue herein, and not the environmental concerns, that is driving long delayed investments by the chemical industry in new biobased silica production plants. The chemical industry is interested in investments whose payback time  $T$  (time required to recover the initial investment  $I$ ) is short, typically 2 or 3 years.<sup>[17]</sup> This requires to maximize the annual cash flow  $C$ , in Eq. (13), and minimize the investment cost:

$$T = I/C \quad (13)$$

Short payback time, however, is one of the two industry's requirements to invest in a new plant-based production route. The other is certainty. Industry, in other words, wants to be certain that sufficient supply of the biological raw material will be available to meet today's and tomorrow's production needs.

The case of highly dispersible, amorphous silica manufactured by RHA meets both all these requirements. More than 715 million tons of paddy rice is harvested annually worldwide each year translating into 480 million tons of milled rice.<sup>[38]</sup> Production is growing, and in 2020/21 the output of milled rice reached the highest level ever of the 526 million tons.<sup>[39]</sup> Rice hulls are about 20 wt% of bulk grain weight, and the ash content by weight in hull is about 25%.<sup>[40]</sup> Hence, some 39 million ton of RHA are available on a global basis, which is a far higher amount than the synthetic amorphous silica world's output of 1.03 million ton comprised of 839,000 ton "wet" silica obtained via Eq. (6) and "dry" silica obtained via flame pyrolytic hydrolysis of  $\text{SiCl}_4$  at  $> 1000$  K affording 4 mol of highly corrosive HCl per mol of silicon tetrachloride (Eq. (14)).<sup>[41]</sup>



Synthetic amorphous silica, finally, sells at a substantially high price of nearly  $\$5 \text{ kg}^{-1}$ . The market indeed amounted to  $\$49$  billion in 2022, projected to grow at nearly 10% annual growth rate until 2030, driven by large demand for tires, but also from construction, personal care and agrochemical industries.<sup>[42]</sup>

It is therefore not surprising to learn that in 2014 a large tire manufacturer announced its intention to replace sand-based silica with biogenic silica from RHA.<sup>[43]</sup> Added to the tire, silica enhances a tire tread's flexibility and elasticity at lower temperatures and improves tires' rolling resistance when compared to carbon black. In 2020, the same company announced it was doubling the amount of biobased SAS used to manufacture part of its tires.<sup>[44]</sup>

In 2023, a large chemical company announced the start of highly dispersible silica for automotive tires production using sodium silicate derived from rice-hull ash as a raw material at its site in Livorno, Italy, by the end of 2024.<sup>[45]</sup> The company would be the first to produce silica from RHA in Europe, where silica-containing tires comprised 67% of passenger tires in Europe already in 1998, but less than 20% in North America<sup>[46]</sup> sourcing RHA from rice milling companies based in northern Italy. The

addition of silica to tire tread reduces the fuel consumption by up to 8% compared to conventional passenger car tires.<sup>[46]</sup>

Similarly, one of the world's leading silica producers announced in late 2022 cooperation with a Thailand-based company burning rice hulls to build a new plant in Thailand that will supply biobased precipitated silica to tire manufacturers.<sup>[47]</sup> Commenting on the initiative, the editors of the rubber trade magazine noted how whereas "sustainable raw materials in tires is increasing significantly, until now only very small quantities of biobased silica are available in the market, which do not meet the rising global demand".<sup>[47]</sup>

## 4. Perspectives and Conclusions

Looking back to what actually drove the commercialization of the biobased route to synthetic amorphous silica after nearly two decades of failed attempts, regardless of its clear economic advantages (burning rice hulls to produce electricity and RHA, generates more energy than required for the overall process), one can clearly recognize in the industrial uptake between 2014 and 2023<sup>[21,43,45,47]</sup> the need for energy efficient tires for battery EVs.

Reviewing the actual development of new biobased production, one can also recognize the typical approach of bioeconomy companies establishing long-term, mutually beneficial relationships with suppliers from the agrifood (or forest) industry.<sup>[48]</sup> Some of these companies are well established chemical companies active in the manufacturing of valued silicon compounds whereas others are new, relatively small companies able to enter the market thanks to the low CAPEX of the biobased route.

The same will happen in the near future for polysilicon production. Now growing at more than 300 GW/a annual rate,<sup>[29]</sup> the photovoltaic technology for electricity production has become a national energy security issue in most world's countries, especially those with the highest population levels and need for low cost electricity.

Production of rice (and thus of rice hulls, the new raw material for silicon-based compounds in the bioeconomy) chiefly takes place in South East Asia, with China, India and Bangladesh being the world's largest manufacturers. Yet, even in the USA the production of rice in 2021 amounted to 8.7 million tons.<sup>[49]</sup> Reliable estimates from the bioenergy practitioners point to an actual availability of 150,000 tons per year of RHA.<sup>[50]</sup> Even a small country such as Italy produces 1.5 million ton of rice every year.<sup>[51]</sup> Another advantage of RHA is that, ~85% silica, it can be safely stored in dry environment. Furthermore, its inherently higher surface area and reactivity overcome the low reactivity of mined silica sources making RHA an ideally suited bioderived raw material for greening the whole silicon-based sector of the chemical industry.<sup>[52]</sup>

In contrast, the production of ultrapure biobased silica from RHA is now a rapidly expanding sector of the chemical industry progressively shifting its raw materials from oil-derived feedstocks to biological resources,<sup>[17]</sup> this is not yet the case for high-purity silicon required for the microelectronic and solar PV

industries. This is not surprising considering the huge investments that took place in South East Asia, and chiefly in China, in polysilicon manufacturing based on conventional chlorosilane-based processes.<sup>[6]</sup>

Said production will not be abandoned, we forecast in conclusion, whereas the supply of  $\text{HSiCl}_3$  will grow thanks to the recently discovered catalytic conversion of  $\text{SiCl}_4$  by-product of the Siemens and Union Carbide processes.<sup>[19]</sup> The major driver for change in polysilicon production occurred since 2004, when dramatic expansion of polysilicon production started in China, is that now the solar cell production rate and installation of solar modules has reached the the 300 GW/a threshold, making PV a crucially important technology for the energy security of most world's countries. This requires to start (or to re-start) polysilicon production for domestic solar cell manufacturing in all major economies: both in the economically developed countries, where it was once produced at small rate for the microelectronic industry, and in rapidly developing large countries in the global South including India, Brazil, the Philippines, Indonesia, South Africa, Nigeria, and Vietnam. Currently, for example, massive uptake of solar PV electricity generation is changing the energy landscape, the practice of agriculture and the living standards in many African countries, from solar street (and home) lighting<sup>[53]</sup> through solar irrigation.<sup>[54]</sup> Africa's countries in 2022 produce over 24 million tons of rice,<sup>[55]</sup> which creates large availability of RHA for use as new raw material for polysilicon manufacturing.

The mere existence of a chemical production technology that is economically viable and truly sustainable (from the environmental, economic and social viewpoints) alone does not mean that the technology will be taken up by industry and commercialized. Especially if, such as in the case of both synthetic amorphous silica and polysilicon, a large and rapidly increasing demand has led suppliers to massively invest in new production capacity using established technology. For the new and lower cost technology to be adopted, *i.e.* for the time must be ripe, the only factors capable of actually driving the shift concern the nature of chemical production in relation for instance to issues of public health or of energy security. The COVID-19 outbreak and disruption in supply chains made clear that no country can rely on imports for essential active pharmaceutical ingredients.<sup>[56]</sup> Similar concepts apply to solar-grade polysilicon, a chemical product which is now essential to the energy security of many world's countries. These powerful, global megatrends that are reshaping the chemical industry and its productions, open the route to the biobased production of both ultrapure silica and ultrapure silicon from an humble agriculture and agrienergy by-product, the ash of rice hull combustion.

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## Conflict of Interests

R.C. and M.P. declare no competing financial interest. R.M. L. as part owner of Mayaterials Inc., also owns I.P. associated with the production of SP.

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