

Mini-Review:**The Potential Perspective of Processing Rice Husk as SiO₂ Source to Tetraalkoxysilane in Indonesia****Benny Wahyudianto¹, Wahyu Satpriyo Putro², Thuy Thi Hong Nguyen¹, Norihisa Fukaya^{2*}, and Sho Kataoka^{1**}**¹Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan²Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan**Corresponding authors:**

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Abstract: Tetra-alkoxysilane (TROS) is one of the useful chemicals and it can be processed to produce semiconductor and photovoltaic devices. Now, the transformation of silica (SiO₂) to TROS is garnering interest due to the potential of extracting it from biomass. As the 14th largest country, Indonesia possesses an abundant source of SiO₂ from mining activities and agricultural waste, notably rice husk (RH). However, only a little concrete action is planned for leveraging RH into a more valuable industrial substance. This review will explain two routes for TROS—conventional and direct—comparing their respective benefits and drawbacks. Additionally, it presents a simulation of various scenarios for scaling TROS production to an industrial level, considering technoeconomic and environmental assessment aspects. The focus then shifts to Indonesia's strategic trajectory for 2045, offering recommendations to enhance resource utilization for economic and national development.

Keywords: Indonesia; rice husk ash; tetra-alkoxysilane

■ INTRODUCTION

Silicon (Si), a semimetal or metalloid, is the second most abundant element in the Earth's crust, constituting 27.72% of its volume [1-2]. Si does not exist in its pure form naturally. It is typically found as silicon dioxide (SiO₂) or as a silicate ion (M₂SiO₃), where M represents cations such as Na, K, or Mg. It is prevalent in materials like silica sand (quartz) and various rocks. Additionally, a small presence of Si is also distributed in plants, well known as one of the beneficial elements, where it is crucial for photosynthetic functions [3]. High SiO₂ concentrations are observed in plants like rice, bamboo, olive, sugarcane, weed, and pine [4]. Specifically, in rice, SiO₂ is concentrated in rice husk (RH) of the paddy, comprising about 20–30 wt.% of the total paddy weight [5-6]. Depending on the plant type and climate, the RH combustion generally produces 20–30 wt.% of rice husk ash (RHA), with SiO₂ as

its main component, approximately more than 80% [7]. Based on direct observations, only a fraction of RHA is currently used for products such as briquettes, fertilizers, and absorbents, with no significant industrial-scale applications targeting RHA for useful chemicals.

Rice is a vital agricultural commodity globally, especially in countries like Indonesia and other Southeast Asian nations. The Food and Agriculture Organization (FAO) of the United Nations reported a total global rice production of 523.1 million tons in 2022/2023 [8-9]. In Indonesia, paddy production reached 54.75 million tons in 2022, making it the third-largest rice producer worldwide (Fig. 1) [10]. It was reported that characteristic of Indonesian RHA contains 87–97% of SiO₂ indicating that the potential SiO₂ amount provided from the total paddy in 2022 is translated into 3 million tons [11]. This amount is ideally

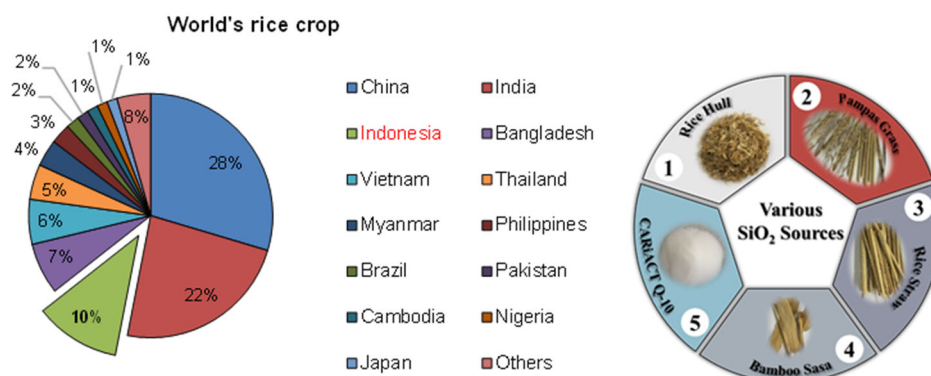


Fig 1. Total production of the world's rice crop and various SiO₂ sources besides rice husk

equals to 1.4 million tons of metallic Si which could cover almost half amount of Si metal demand in global market (3.50–3.75 million tons) [12]. It is clearly shown that Indonesia has a great potential to produce SiO₂ from its natural RH. The remaining amount could be covered from rice hulls, pampas grass, rice straw, and bamboo which are also notable SiO₂ sources. Despite being one of the largest RHA producers globally, the variety of products derived from it in Indonesia is limited. Si materials are widely used in several applications, including photovoltaics in smart devices (photovoltaics) [13–15], anode [16], useful chemicals [17], concrete [18–20], and so on. However, these high-value products require extensive processing, including carbothermal or metallothermic reduction, refining, and methods like the Siemens or Union Carbide process, to achieve metallurgical or solar-grade Si.

From several application examples, Indonesia has the potential to transform RH, a waste material from rice, into useful chemicals such as tetra-alkoxysilane (TROS), thereby accelerating economic benefits [21]. This brief review will discuss TROS synthesis at a laboratory scale, including techniques to optimize TROS yield. Additionally, it will cover scaling up TROS production

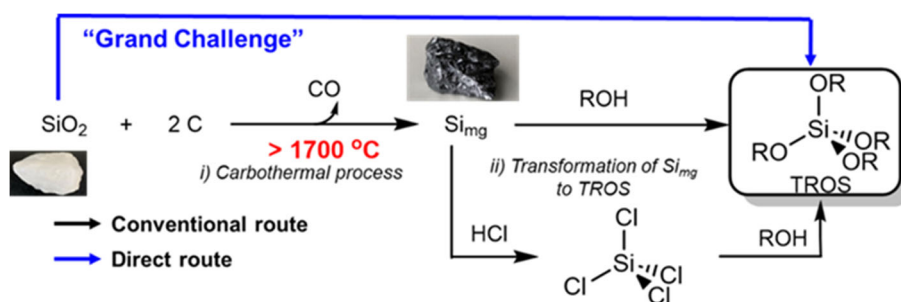
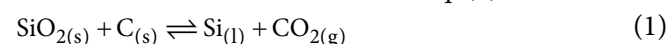
using scalable simulations and conclude with recommendations for the Indonesian Government to capitalize on current and potential market opportunities.

■ CONVENTIONAL ROUTE

The conventional route is a method for producing metallurgical grade silicon (Si_{mg}) on a large scale, typically employed when the raw material is derived from mining, such as silica-rich rock or sand. TROS production via the conventional route involves two main processes: (i) converting SiO₂ to Si_{mg} through the carbothermal process and (ii) converting Si_{mg} to TROS by adding alcohol (Scheme 1).

Carbothermal Process

Carbothermal reduction is a traditional method for obtaining Si_{mg}, requiring high temperatures (> 1700 °C). The process begins with the addition of carbon to SiO₂, initiating a reaction where carbon reacts with the oxygen atoms in SiO₂ to produce CO₂ and liquid silicon; Si_(l). The chemical reaction is shown in Eq. (1).

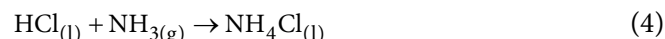
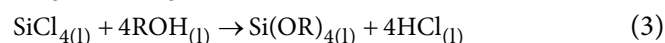


Scheme 1. Roadmap of this review

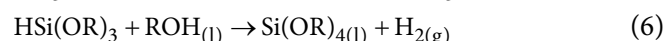
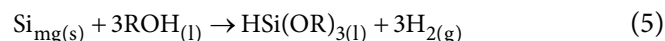
The resulting $\text{Si}_{(l)}$ is then shaped through solidification and classified by size. Concurrently, CO_2 is released as a byproduct. Literature suggests that producing 1 kg of Si_{mg} consumes approximately 1.5 L of gasoline, resulting in over 30 Mt of CO_2 emissions [22-23]. The generation of CO_2 , a greenhouse gas (GHG), poses a significant environmental concern. Moreover, these emissions may be subject to carbon taxation or cap-and-trade systems per ton [24-26]. Consequently, there is a growing interest in alternative methods that minimize environmental impact while maximizing industrial profit. The reactor illustration is shown in Fig. 2 [27-28].

Transformation from Si_{mg} to TROS

Over a century ago, TROS synthesis involved chlorine gas (Cl_2) to produce SiCl_4 . Following the carbothermal process, Si_{mg} is exposed by Cl_2 to form SiCl_4 as an intermediate. SiCl_4 is then reacted with alcohol, resulting in TROS. However, this method produces HCl as a byproduct, which poses toxicity concerns, although it is neutralized by NH_3 in the purification process. The stepwise reactions are illustrated in Eq. (2-4):



In pursuit of green chemistry and sustainability, newer methods have been developed to substitute Cl_2 in the reaction, utilizing an excess of alcohol. The most important reactions were shown in Eq. (5-6).



Despite the complexity and potential for side products in reactions (5) and (6), they are considered more environmentally favorable than the older method using Cl_2 [29-31]. To the best of our knowledge, only a limited number of studies have documented the conversion of Si_{mg} to TROS using direct alcohol. The substrate scope of aliphatic alcohols $\text{C}_n\text{H}_{2n+1}$ with $n = 1-4$ is detailed in Table 1, featuring tetramethyloxysilane (TMOS), tetraethyloxysilane (TEOS), tetrapropyloxysilane (TPOS), and tetrabutoxysilane (TBOS) for $n = 1, 2, 3$, and 4, respectively.

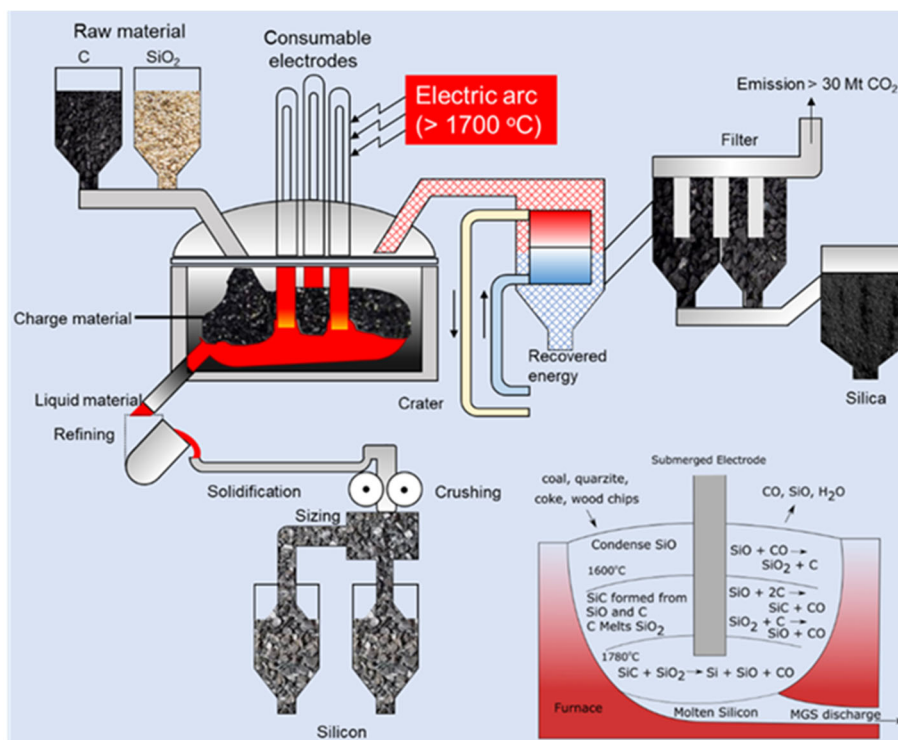


Fig 2. Scheme of carbothermal reactor

Table 1. TROS production from Si_{mg} using several methods

Alcohols (Product)	Temp. (K)	Time (h)	Yield (%)	Special treatment	Ref.
MEOH (TMOS)	523	3	88.0	inside steel autoclave	[29]
	533	3	89.0	inside steel autoclave	[29]
EtOH (TEOS)	448	9	70.6	with diethylene glycol monoalkyl/Na cat.	[30]
	533–543	4–5	15.5	onto Si/Cu mixture	[31]
<i>n</i> -PrOH (TPOS)	523	3	84.0	inside steel autoclave	[29]
	563–593	4–5	4.8	onto Si/Cu mixture	[31]
<i>n</i> -BuOH (TBOS)	523	3	96.0	inside steel autoclave	[29]

Table 2. TEOS production at different temperatures using a Roth Model II autoclave [29]

Temperature (K)	Conversion (%)	Selectivity (%)
513	67	90
523	77	80
533	71	89
543	82	91

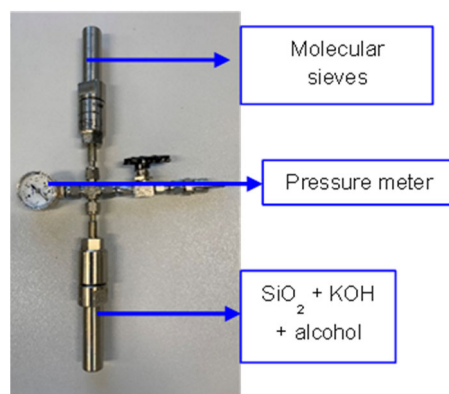
The production of TROS from Si_{mg} and alcohol is achieved using various techniques, yielding a range of results. As demonstrated in Table 1, significant yields of TROS are attainable even without the consumption of Cl_2 [29–30]. This approach allows for the omission of the neutralization step for HCl and NH_3 . Among the methods tested, the use of an autoclave has shown consistently high yields across different alcohols, ranging from 70% to 96% [29]. The autoclave's advantages extend beyond yield, offering simplicity, environmental friendliness, safety, and efficiency. Furthermore, the conversion reactions within the autoclave under varying temperatures have been evaluated and are documented in Table 2. One advantage of using an autoclave is the capability to conduct reactions at elevated temperatures and pressures [32]. As evidenced in Table 2, increasing the reaction temperature boosts the conversion of Si to TEOS, although selectivity remains relatively constant.

Overall, TEOS production from mining involves a longer process due to the indirect nature of converting silica-rich materials to TROS. Producing TROS from such sources requires high energy input, particularly during the carbothermal process, where SiO_2 transforms to Si_{mg} under high temperatures. Additionally, continuous mining may threaten local ecosystems and diminish the natural state of the area. Consequently, our team is motivated to develop a safer, simpler reaction condition

for direct TROS production from the corresponding SiO_2 source.

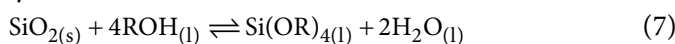
■ DIRECT SYNTHESIS ROUTE (TRANSFORMATION OF SiO_2 TO TROS)

Recently, green synthetic pathway considered as a ‘grand challenge’ was discovered by Fukaya et al. [33] using direct organic waste of RHA and alcohol. Through their finding, the method is promising as it could replace more hazardous processes and eliminate drawbacks associated with the conventional route, such as high-temperature reactions and the use of harmful chemicals. In their investigation, the key factor for successive TROS production in a high yield is the innovative reactor design, which segregates the reaction site and the dehydrating vessel containing MS. (Fig. 3). This setup ensures that water molecules produced during the reaction evaporate due to high temperatures. In the upper valve, water molecules are removed by the dehydrating agent, allowing the remaining reactants to transform into TEOS without interference. This separation is crucial, as TROS is also a dehydrating agent

**Fig 3.** Schematic representation and picture of the reaction apparatus

and could otherwise compete with water, inhibiting the reaction's progress.

The chemical reaction for synthesizing TROS through direct route is represented in Eq. (7). To the best of our knowledge, current literature on direct TROS synthesis is limited, with most studies listed in Table 3.



The starting material for SiO_2 can be either natural waste such as RHA or synthetic reagents like CARiACT Q-10 (Table 3). Typically, the preparation of TROS using aliphatic alcohol $\text{C}_n\text{H}_{2n+1}\text{OH}$ ($n = 1-4$) produced a high yield. Even though, other types of alcohol can be designed to synthesize cyclic TROS for certain purposes [36-44]. Surprisingly, the use of RHA as natural SiO_2 source produced a higher yield of TMOS (68%) than CARiACT Q-10 (48%). The yield of TEOS was slightly decreased to 60% when RHA was used indicating the potential use of RHA for this reaction system. Without a dehydrating agent, TEOS yield decreases significantly during the reaction process (Ref. [33]), while the presence of molecular sieves 3A as the dehydrating agent generates

more TEOS (3% vs. 70%) under the same conditions. The existence of water molecules present during the reaction shifts the equilibrium toward the reactant side, hindering TROS formation. By trapping them to dehydrated agent, the reaction undergoes normally to generate more TROS as a desired product. Further improvements were made by using longer alcohols, such as *n*-propanol or *n*-butanol, resulting in yields of 73% for TPOS and 79% for TBOS. These results emphasize the critical role of water removal in enhancing TROS production. Further investigations focus on various aspects, including the pore size of dehydrating agents, recyclability of the reaction system, the calcination effect on SiO_2 substrates, and life cycle assessment analysis.

Pore Size of Dehydrating Agent

The efficiency of commercially available dehydrating agents is significantly influenced by their pore size, which affects their interaction with active sites. Fukaya et al. [33] assessed the impact of dehydrating agent pore size on TEOS yield, as shown in Table 4.

Table 3. TROS production from SiO_2 using several methods

Silica sources	Alcohols (Product)	Temp. (K)	Pressure (MPa)	Time (h)	Yield (%)	Additives	Ref.
CARiACT Q-10	MeOH (TMOS)	513	2 (CO_2)	24	49	2,2-dimethoxypropane (dehydrating agent), KOH (cat.)	[34]
RHA	MeOH (TMOS)	513	2 (CO_2)	24	68	2,2-dimethoxypropane (dehydrating agent), KOH (cat.)	[35]
RHA	EtOH (TEOS)	533	—	6	60	Molecular sieves 3A (dehydrating agent), KOH (cat.)	[31]
CARiACT Q-10	EtOH (TEOS)	533	—	6	3	KOH (cat.)	[33]
CARiACT Q-10	EtOH (TEOS)	533	—	6	70	Molecular sieves 3A (dehydrating agent), KOH (cat.)	[33]
CARiACT Q-10	<i>n</i> -PrOH (TPOS)	533	—	6	73	Molecular sieves 3A (dehydrating agent), KOH (cat.)	[33]
CARiACT Q-10	<i>n</i> -BuOH (TBOS)	533	—	6	79	Molecular sieves 3A (dehydrating agent), KOH (cat.)	[33]

Table 4. Effect of pore size of molecular sieve [33]

Molecular sieves	Pore diameter* (nm)	TEOS (%)	Disiloxane (%)
3A	0.3	70	16
4A	0.4	54	14
5A	0.5	32	9
13X	1.0	50	13

The reaction conditions were the same as those in Table 3

*Average pore diameter taken from ref. [45]

The findings reveal that an increase in pore diameter (comparing molecular sieve 3A, 4A, and 5A) generally leads to reduced SiO₂ conversion and TEOS production. Yet, the pattern becomes inconsistent upon introducing the 13X (zeolite) dehydrating agent, indicating that the structure and cations of the dehydrating agent also affect its performance.

Recyclability of the Reaction

Molecular sieve 3A was identified as the most effective in preparing TROS, as indicated in Tables 3 and 4. The study further investigated the recyclability of molecular sieve 3A [33] which is critical for transitioning the reaction from the laboratory to the industrial level. They reused the same molecular sieve 3A for multiple TEOS production cycles, regenerating deactivated sieves by heating them at 300 °C under vacuum for 15 h. As shown in Table 5, the results demonstrate that the dehydrating agent retains efficacy for at least 6 cycles without performance degradation, indicating good recyclability for TEOS (or TROS) production.

The Calcination Effect and Size of Silica

The final aspect examined is the use of RH as an organic waste SiO₂ source, focusing on the calcination process. By varying the calcination temperature between 500–1000 °C for transforming RH into RHA, they observed changes in surface area through BET analysis. Higher calcination temperatures tended to result in smaller surface areas, which significantly impact the yield. As detailed in Table 6, the sample “RHA-500” exhibited the highest effectiveness, producing a 60% yield of TEOS. However, a notable drawback was the concurrent production of disiloxane (DS) as a byproduct. Therefore, temperature serves as a crucial variable (trade-off) in

maximizing TEOS yield while minimizing undesirable byproducts. The study compared the surface area’s impact on TEOS production was also evaluated by Fukaya et al. [33] by using quartz and celite 209 with narrow contact surface. Both substrates show insignificant SiO₂ conversion, like RHA-1000. This result exhibited a strong correlation between surface area and TEOS yield through direct synthesis. For practical industrial application, the study explored scalability, increasing substrate volume tenfold and slightly reducing the reaction temperature from 260 to 240 °C. Remarkably, the yield of TEOS reached 70% during a 6 h reaction on a semi-industrial scale. This finding underscores a promising route to mass-producing TEOS, marking a significant step toward industrialization.

We have delineated the production of TROS through both conventional and direct synthesis methods, each presenting its own set of advantages and limitations. The conventional method, while suitable for mass production, has environmental and energy-intensive issues, particularly due to continuous mining.

Table 5. Recyclability of molecular sieve 3A [33]

Number of cycles	TEOS (%)	Disiloxane (%)
1 (fresh)	70	16
2	78	15
3	80	15
4	79	15
5	84	15
6	81	14

The reaction conditions were the same as those shown in Table 3

Table 6. TEOS production from natural silica substrate at variant temperature [33]

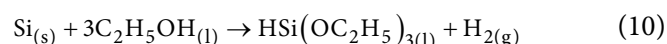
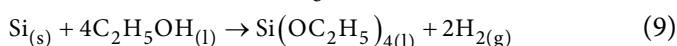
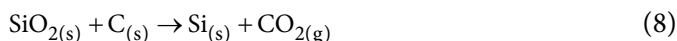
Silica	$a_{s,BET}$ (m ² g ⁻¹)	TEOS (%)	Disiloxane (%)
RHA-500	224	60	11
RHA-600	202	57	8
RHA-700	135	44	10
RHA-800	28	41	3
RHA-900	3	11	0
RHA-1000	0.6	6	0
Quartz	0.8	3	0
Celite 209	1	5	0

The reaction conditions were the same as those shown in Table 3

Conversely, the direct method facilitates the conversion of SiO₂ from organic waste such as RHA into TROS with a high yield and is recognized as green chemistry. However, scaling this method to mass production levels remains a challenge, as the most extensive trial to date utilized less than 1 kg of substrate. Therefore, a thorough simulation or technoeconomic analysis is necessary for an initial evaluation before committing to large-scale manufacturing.

Life Cycle Assessment

One year after the initial study, Nguyen et al. [46] conducted a technoeconomic and environmental assessment for optimizing TEOS production, utilizing the Pro/II simulator. They compared the existing scenario with 4 alternative approaches based on the direct synthesis method, as detailed in Table 7 [33,46-47]. Base case is used Si_{mg} which obtained from silica-rich resources, such as quartz. The chemical reaction for Si_{mg} production is written in Eq. (8-10). The reduction is placed in an electric furnace at 1900 °C using carbon (i.e., coke, charcoal, or wood chip) as a reducing agent, and the Si_{mg} is then used for TEOS production. The base case involved using Si_{mg} derived from silica-rich resources like quartz. The chemical reactions for Si_{mg} and TEOS production are outlined in Eq. (8-10), with reduction occurring in an electric furnace at 1900 °C using carbon (such as coke, charcoal, or wood chip) as the reducing agent. The study also examined a new route proposed by Fukaya et al. [33], involving RHA-500 and molecular sieves 3A as the dehydrating agent.



All processes are designed to produce high-purity TEOS (99.5%) at a maximum capacity of 1000 tons/year. Key distinctions were in temperature conditions (180 °C for conventional vs. 240 °C for the new route), SiO₂ sources (Si_{mg} for conventional vs. biogenic SiO₂ for the new route), and the SiO₂ source/ethanol ratio. Table 7 indicates that alternative 1 (Alt. 1) is the most effective reaction simulation, with substrate conversion reaching 96% and TEOS production up to 91%. The byproduct formation was only 2.8%, as shown in Eq. (10). However, this alternative required a significant excess of ethanol compared to Alt. 2-4. The conventional route showed moderate Si_{mg} conversion (88%), good TEOS production (74%), and 4.86 times less ethanol consumption. Despite its effectiveness, the conventional route is more energy-intensive due to the high temperatures needed for Si_{mg} production. The results in Table 7 suggest that the method developed by Fukaya et al. [33] could potentially replace the conventional route due to its lower energy requirements, environmentally friendly approach, and simpler reactor design. Nonetheless, the optimal utilization of excess ethanol to generate more TROS with efficient alcohol consumption remains a consideration.

Further investigation by Nguyen et al. [46] involved calculating simulations of the total production cost (in USD) for all alternatives and comparing these to conventional processes (Fig. 4). The total production cost shown in Fig. 4 is the sum of operating cost, including raw material and utility costs, and equipment cost, in which the former dominates the latter. The operating cost is overweighted by the raw material cost. As shown in Table 7, the amount of ethanol input to the

Table 7. Reaction conditions included in the base case and new synthesis routes [46]

	Base case	Alt. 1	Alt. 2	Alt. 3	Alt. 4
Temperature (K)	453	513	513	513	513
Key input component	Si metal	Biogenic SiO ₂	Biogenic SiO ₂	Biogenic SiO ₂	Biogenic SiO ₂
Key component: EtOH	1:23	1:112	1:57	1:37	1:28
Main by-product	TRES*	DS	DS	DS	DS
Conv. (%)	88.0	96.9	77.2	82.0	70.7
TEOS (%)	74.0	91.3	68.0	56.2	44.8
By-product (%)	14.0	2.8	4.6	12.9	12.9

*TRES: triethoxysilane

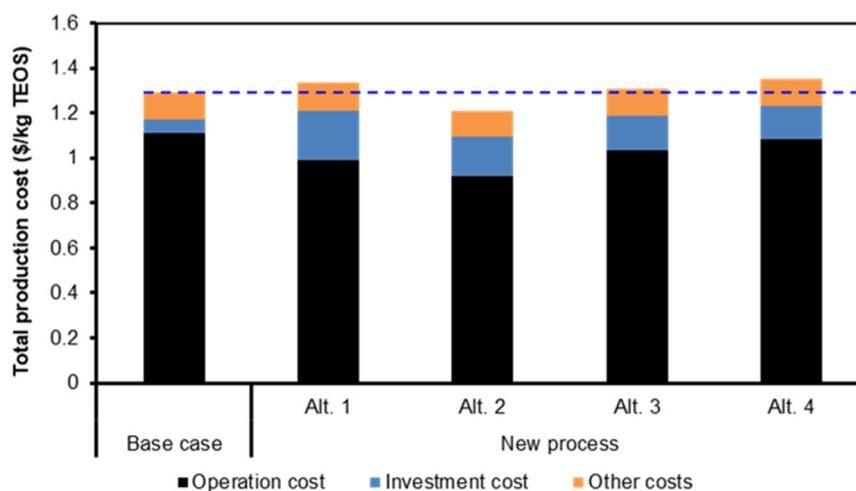


Fig 4. Comparing the total production cost of the base case versus the new process

base case is much lower than that input to the Alt. 2. As a result, the energy amount required for recovering unconverted ethanol after the synthesis in the base case is lower. However, in the base case process Mallon et al. [47], a much larger amount of by-product is produced (as shown in Table 7, 14% of Si_{mg} conversion). Thus, in the base case, much large amounts of Si_{mg} and ethanol are lost due to reaction (10), resulting in extremely high raw material consumption cost. Consequently, the Alt. 2 has a lower total production cost than the base case.

The base case process was evaluated using different electricity sources, which have markedly different life cycle GHG emissions, as shown in Fig. 5 [46]. As

evaluated by Hondo et al. [48], electricity's life cycle GHG emission amount becomes the highest when coal is used for electricity generation. This amount reduces when other sources, e.g., fuel oil, natural gas, renewable energy, etc., are used. In the base case process, the main input raw material is Si_{mg} , the production of which requires extremely high amount of electricity (approximately up to 13,000 kWh/ton Si_{mg}). Thus, the base case process' total GHG emission amount changes when the electricity source used for Si_{mg} production changes. The new process uses SiO_2 as the main input raw material, which is obtained from incinerating carbon-neutral biomass resources. So, compared with the

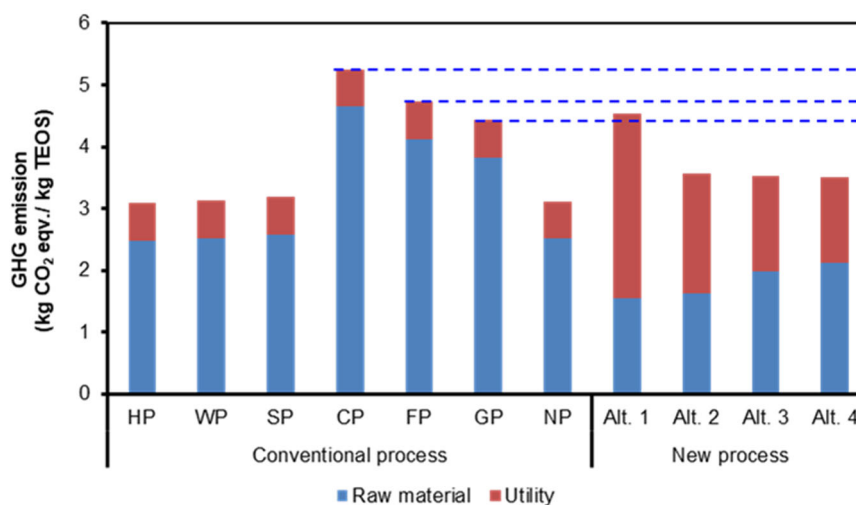
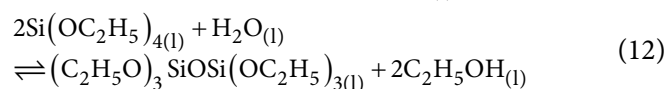
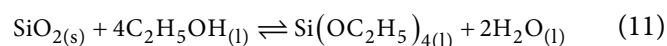


Fig 5. Comparison of GHG emissions from conventional and new processes. CP: coal power; FP: fuel oil power; GP: liquefied natural gas power; NP: nuclear power; HP: hydropower; WP: wind power; SP: solar-photovoltaic power

base case process, the new process can help reduce a large amount of GHG emissions. This reduction amount varies depending on the source of electricity the base case uses. The new process, particularly in configurations other than Alt. 1, can reduce GHG emissions by 34%, 26%, and 21% for electricity derived from coal, fuel oil, and liquefied natural gas, respectively. Conversely, replacing these with renewable energy sources like hydropower, wind power, and photovoltaic power results in the base case emitting marginally less in terms of global warming potential compared to the new process.

In a subsequent study, Nguyen et al. [49] explored the impact of various dehydrating agents on TEOS production, examining materials such as CaCl_2 , MgSO_4 , Na_2SO_4 , CaO , and molecular sieve 3A, as outlined in Table 8. Notable findings from Table 8 include the significantly low TEOS yield in control experiments without dehydrating agents, where the reaction favors the reactants. Metal salts such as CaCl_2 , MgSO_4 , and Na_2SO_4 showed poor performance in binding water molecules. In contrast, CaO effectively adsorbs water, particularly with increasing ratios of dehydrating agent to SiO_2 . This efficiency of CaO removes the need for specialized reactors, unlike the custom reactor required by the method of Fukaya et al. [33]. Additionally, the use of CaO helps reduce the formation of byproducts, as TEOS can react with existing water molecules to form hexaethoxydisiloxane (HEDS), as indicated in Eq. (11–12).



CaO can be regenerated as a dehydrating agent by heating the saturated material at 850 °C for 6 h, whereas molecular sieve 3A requires regeneration at 300 °C under vacuum for 15 h [33]. This distinction informs the design of 2 alternative reactors for TEOS production, each utilizing either molecular sieve 3A or CaO as the dehydrating agent. The placement of these agents is fundamentally different, molecular sieve 3A is segregated (*ex-situ*) from the main reactor to prevent the disruption of silica-alumina interactions, while CaO can be mixed with reactants in a heterogeneous system (*in situ*).

Nguyen et al. [21,46] further assessed production costs and GHG emissions based on simulation studies, comparing previous data with new alternative scenarios (Fig. 6). The terms “ Si_{mg} process” and “silica process” represent conventional and direct routes, respectively. Scenarios 1 and 2 involve utilizing excess energy from steam generation and the cogeneration of steam and electricity, respectively, to reduce production costs associated with heating equipment [21]. The Si_{mg} process is associated with higher production costs and GHG emissions compared to the SiO_2 process, indicating the latter’s superior efficiency and environmental sustainability. Scenario 1 offers a significant reduction in

Table 8. Result of TEOS synthesis from SiO_2 and ethanol [49]

Method of DA	Entry	Process	DA ^b	Ratio M: SiO_2 ^c	TEOS (%) ^d	DS (%) ^d
<i>In situ</i> ^a	1		None		4.0	0.0
	2		CaCl_2	3:1	Trace	0.0
	3		MgSO_4	3:1	2.0	0.0
	4		Na_2SO_4	3:1	4.0	0.2
	5	Alt. 1	CaO	1:1	25.9	3.2
	6	Alt. 2	CaO	2:1	48.8	7.0
	7	Alt. 3	CaO	3:1	75.9	2.0
	8	Alt. 4	CaO	4:1	63.0	1.7
	9	Alt. 5	CaO	5:1	62.1	0.6
<i>Ex situ</i>	10	MS process	MS 3A		68.0	4.6

^aReactions were performed using SiO_2 (9.0 mmol), the dehydrating agent, and KOH (0.9 mmol) in EtOH (24 g); ^bDA = dehydrating agent; ^cMolar ratio of the metal of the dehydrating agent (M) and SiO_2 used in the reaction; ^dTEOS (tetraethyl orthosilicate) and DS (disiloxane) yields were determined by GC using *p*-tert-butyltoluene as the internal standard with yield = moles of product formed/moles of SiO_2 introduced in the reactor

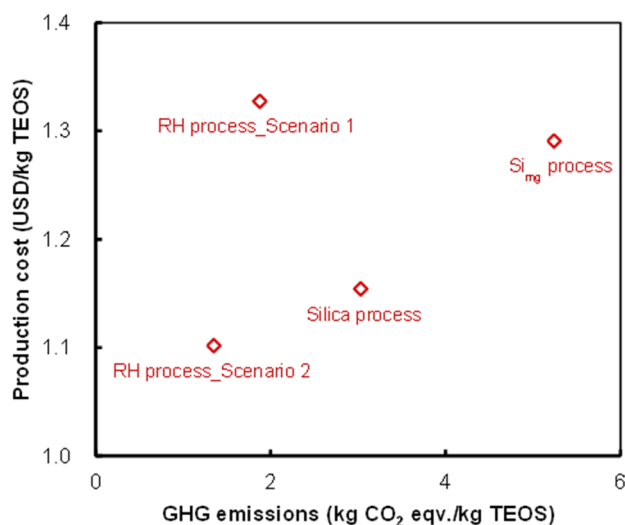


Fig 6. Production cost vs. CO₂ emissions

GHG emissions, whereas scenario 2 is more effective as it reduces both GHG emissions and production costs. These findings underscore the importance of considering GHG emissions, especially in light of potential CO₂ tax policies that might impose taxes ranging from 0 to 150 USD per ton on emissions [50].

CONCLUSION

Currently, the preparation of RHA to TROS becomes safer and more feasible using the direct route with alcohols instead of Cl₂ gas, as employed in the conventional route. This new methodology significantly reduces energy consumption and the production of undesired byproducts, marking a considerable advancement in converting biomass waste into high-demand products. Ongoing mass production research, including technoeconomic assessments, suggests several alternatives for realizing industrial-scale TROS production in an environmentally sustainable manner according to recent regulations. Technoeconomic analysis indicates that the new process could reduce total production costs by 7% and GHG emissions by 34% compared with the conventional method, while meeting the high demand for TROS as a precursor for advanced materials. Considering the findings of new technology for TROS production and RHA availability stock in Indonesia, we recommend Indonesia's government to consider the opportunity by adding and prioritizing this plan into Indonesia Trajectory 2045. For that purpose, the design of the laboratory and implementation

in the industry must comply with both Indonesian and international regulations to ensure a suitable and legal research environment. This adherence will facilitate not only the development of environmentally friendly processes but also the commercial viability and acceptance of the produced chemicals. Moreover, technoeconomic assessments showed that the direct synthesis route offered lower production costs and reduced GHG emissions. This aligns with minimizing pollution and adhering to sustainable development goals. The impacts will be felt by many parties, including the government, industries, academic sector, high and low-skill labor, and local communities if this opportunity can be realized with good sustainability.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Benny Wahyudianto conducted conceptualization, writing, reviewing, and editing the original paper. Wahyu Satpriyo Putro conducted conceptualization, writing, reviewing, and editing the original paper. Thuy Thi Hong Nguyen conducted conceptualization, reviewing, and editing the original paper. Norihisa Fukaya conducted conceptualization, reviewing, and editing the original paper. Sho Kataoka conducted conceptualization, reviewing, and editing the original paper. All authors agreed to the final version of this manuscript.

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