Green Chemistry

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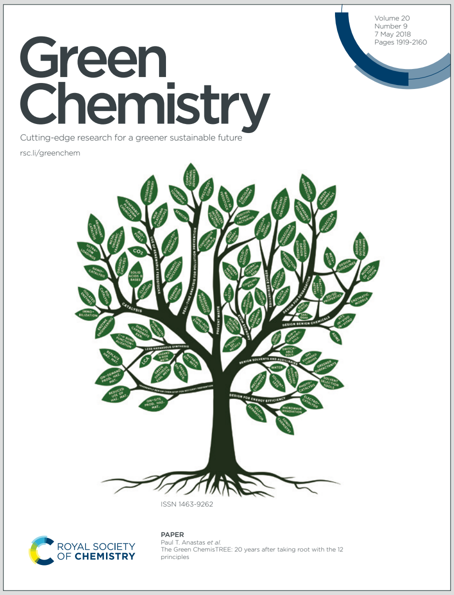

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1. This work advances green chemistry by integrating benchmark and prospective life cycle assessment (LCA) to quantitatively evaluate silicone elastomers and emerging recycling technologies, linking molecular processes with environmental performance
2. A key achievement is the identification of emission drivers and quantification of recycling benefits: base-catalyzed depolymerization reduces greenhouse gas emissions of PDMS to 1.83 kg CO_2 eq/kg and enables up to 55 % reduction in silicone sealant emissions. The study also reveals critical roles of energy source, solvent use, and process yields.
3. Further improvements require reducing solvent demand, avoiding stoichiometric reagents, and integrating renewable energy. Future research should focus on scalable low-temperature processes, improved solvent recycling, and inclusion of waste collection impacts to enable fully circular silicone value chains

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ARTICLE

Closing the Loop on Silicone Elastomers: Life Cycle Evaluation of Virgin Materials and Recycling Processes

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Silicone elastomers are widely used materials whose production is energy-intensive and reliant on fossil-based precursors. This study evaluates their environmental impacts through a combined life cycle assessment (LCA) and prospective LCA, covering both virgin production and five chemical recycling routes. The cradle-to-gate greenhouse gas (GHG) emissions of a representative room-temperature-vulcanizing (RTV-1) silicone sealant were quantified as 5.79 kg CO_2-equivalent (CO_2 eq.) per kilogram, dominated by poly(dimethylsiloxane) (PDMS) synthesis (82 %). Prospective LCA of recycling technologies, including base-, acid-, fluoride-, and metal-catalyzed depolymerization, as well as thermal depolymerization, revealed strong dependencies on reaction temperature, solvent use, and stoichiometric reagents. Among the assessed routes, potassium hydroxide–catalyzed depolymerization showed the lowest GHG emissions (1.83 kg CO_2 eq. per kilogram of regenerated PDMS). Incorporating recycled PDMS into RTV-1 formulations can reduce product-level emissions by up to 55 %. Sensitivity analyses demonstrated that thermal energy sources and solvent recycling, particularly in fluoride- and boron-based processes, substantially influence environmental outcomes. Overall, the results highlight that chemical recycling can significantly reduce the environmental footprint of silicone elastomers and represents a viable strategy for enabling a more circular and sustainable silicone materials value chain

1. Introduction

Silicones are organosiloxane polymers that have become ubiquitous in modern life, with applications spanning household products to advancedtechnical sectors. The global silicone market is projected to exceed 19 billion dollars by 2025, with elastomers representing the largest segment at 37.6 % of total volume.[1]

Owing to their versatile chemistry, silicone polymers can be readily converted into three-dimensional networks through condensation, addition, or radical crosslinking reactions.[2]

Consequently, silicone elastomers typically incorporate reactive silanes or functionalized polymers designed to enable these crosslinking processes.

Within the important subclass of one-component room-temperature vulcanizing silicones (RTV-1), crosslinking occurs through moisture-induced hydrolysis, generating volatile by-products and silanols that subsequently undergo further condensation to form the elastomeric network.[3] This reaction can be catalyzed by acids, bases, or organometallic compounds (most notably organotin complexes) to efficiently yield a robust three-dimensional structure.[4] An overview of the key components used in RTV-1 silicone formulations and their respective functions is provided in Table 1.[3a, 5]

Table 1. Components of RTV silicones and their function.[3a]

Component	*Chemical Nature*	*Function*
Polymer	HO-[$SiMe_2$-O]$_n$-H	Backbone of the elastomeric network
Plasticizer	Me_3-Si-[O-$SiMe_2$]$_n$-Me	Adjustment of mechanical properties
Cross-linkers	Acetoxy X-Si(OC(O)CH_3)$_3$ Alkoxy X-Si(OR)$_3$ Oxime X-Si(ON=CRR´)$_3$ Amine X-Si(NHR)$_3$ Ester X-Si(ORC(O)OR´)	Binding between single polymer chains to form the three-dimensional network
Fillers	Fumed Silica (SiO_2) Chalk	Cohesion promoter, provides toughness to the elastomer
Adhesion Promoter	X-CH_2CH_2-Si(OR)$_3$	Improve the adhesive properties on different substrates
Catalyst	Organo -Sn, -Ti, -Pt, -Zn, -Rh	Enabling / acceleration of the curing

1.1 Direct Synthesis of Silicones

The precursors of all commercial silicones are methylchlorosilanes, primarily dimethylchlorosilane (DMCS), which are produced via the so-called “direct synthesis.” This process was independently discovered in the 1940s by R. Müller

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in Radebeul[6] and E. G. Rochow at General Electric Co.,[7] and is therefore commonly referred to as the Müller–Rochow process. In this reaction, a gaseous mixture of hydrogen chloride and chloromethane is passed over a Si/Cu alloy at approximately 370 °C, a procedure that has since become the industrial standard for silicone manufacturing.[8] The silicon required for the Müller–Rochow process is typically produced through the carbothermic reduction of quartz at around 2000 °C.[9] China currently dominates global production, with an estimated 6 million metric tons of silicon manufactured in 2021.[10] To obtain the polydimethylsiloxanes (PDMS) used in silicone elastomers, the resulting methylchlorosilanes undergo distillation, hydrolysis, and subsequent polymerization.

The linear, fossil-based value chain of today's silicone industry increasingly contributes to raw material constraints, environmental pollution, and significant greenhouse gas (GHG) emissions.[11] Given the unique performance characteristics of silicones, including thermal and chemical stability, optical clarity, and the absence of odor, current sustainability strategies aim to reduce environmental impacts by emphasizing reuse and recycling of silicone materials rather than seeking their wholesale replacement.[3a, 12]

1.2 Chemical Recycling of Silicones

Silicone depolymerization methodologies mostly rely on the partially ionic character of siloxane bonds, which increases their reactivity toward strong electrophiles or nucleophiles. As a result, thermal or thermochemical depolymerization can occur between room temperature and 600 °C depending on the catalysts, reactants, and conditions employed.[13] This broad range may be divided into three temperature regimes:

- Low temperature (20–180 °C): strongly acid- or base-catalyzed depolymerization;
- Medium temperature (180–350 °C): weak Lewis acid or base catalysis;
- High temperature (350–600 °C): purely thermal depolymerization.

The mechanisms underlying silicone depolymerization have been studied extensively in recent years, with further detail available in recent reviews by our group[14] and by Furgal[15] (Figure 1). For this study, we focus on industrially relevant, low-temperature recycling processes capable of producing chlorosilanes or siloxanes suitable for reinsertion into the existing silicone value chain. Other emerging approaches (such as alcoholysis, aminolysis, acetylation, fluorination, and organic base-mediated depolymerization) are acknowledged but not considered further here. Other innovative strategies to improve silicone performance, processability or debonding have not been considered either.

Industrial efforts to recover valuable monomers typically center on Brønsted acids and bases at low temperatures, halogen-containing depolymerization agents, and high-temperature thermal polymer degradation, the latter valued for its simplicity and low monomer contamination. Brønsted acid-catalyzed depolymerization has been shown to produce cyclic siloxanes at 70–250 °C using sulfuric acid[16] as the most common catalyst, with additional examples employing hydrochloric acid,[17] acetic acid,[18] sulfonic acids,[19] or triflic acid.[16a] Brønsted base catalysis likewise yields cyclic siloxanes at 110–200 °C using alkali metal hydroxides such as potassium[20] or sodium hydroxide,[21] as well as tetramethylammonium hydroxide.[22] Halogen-containing depolymerization agents can generate the corresponding halomethylsilanes at 25–100 °C when combined with other catalysts, for example using boron trifluoride,[23] carboxylic acid chlorides,[24] or boron trichloride.[25] Finally, fluoride-mediated depolymerization enables the formation of cyclic siloxanes at room temperature using tetrabutylammonium fluoride (TBAF) in organic solvents.[26]

1.3 Life Cycle Assessment of Silicones

To quantitatively assess the environmental impacts of products and emerging technologies, the life cycle assessment (LCA) methodology is widely employed. In an LCA, all relevant material and emission flows are identified, quantified, and evaluated across multiple impact categories.[27] Comparative LCAs are particularly valuable when assessing several processes that yield the same product, enabling a robust comparison to the current state of the art. For technologies that have not yet reached industrial maturity, prospective LCA approaches allow meaningful environmental evaluations by linking lab-scale data to anticipated industrial-scale performance. Such prospective assessments help identify major emission drivers, highlight early-stage optimization opportunities, and guide scale-up decisions.[28] Although methodological limitations and uncertainties remain, especially regarding absolute values, comparisons at consistent scales have proven to be powerful tools for technology development.[29]

The aim of this study is to quantify the environmental impacts of commercial, fossil-based RTV-1 silicones as the state-of-the-art benchmark, providing a prospective, quantitative framework for evaluating emerging recycling technologies at an early stage.

Thus, from each class of chemical recycling strategies mentioned in Section 1.2, one representative process was selected for detailed modelling and comparison. Following the description of the LCA methodology, we present the benchmark assessment of commercial moisture curing RTV-1 materials, followed by the comparative prospective LCA of the selected recycling routes. A sensitivity analysis then examines the influence of thermal energy sources and organic solvent recovery, and overall uncertainty is further evaluated through Monte-Carlo simulation.

.Building on this baseline, the prospective LCA is used to evaluate the potential and feasibility of different chemical silicone recycling technologies that regenerate monomers suitable for reintegration into the silicone value chain, thereby supporting a more circular economy.

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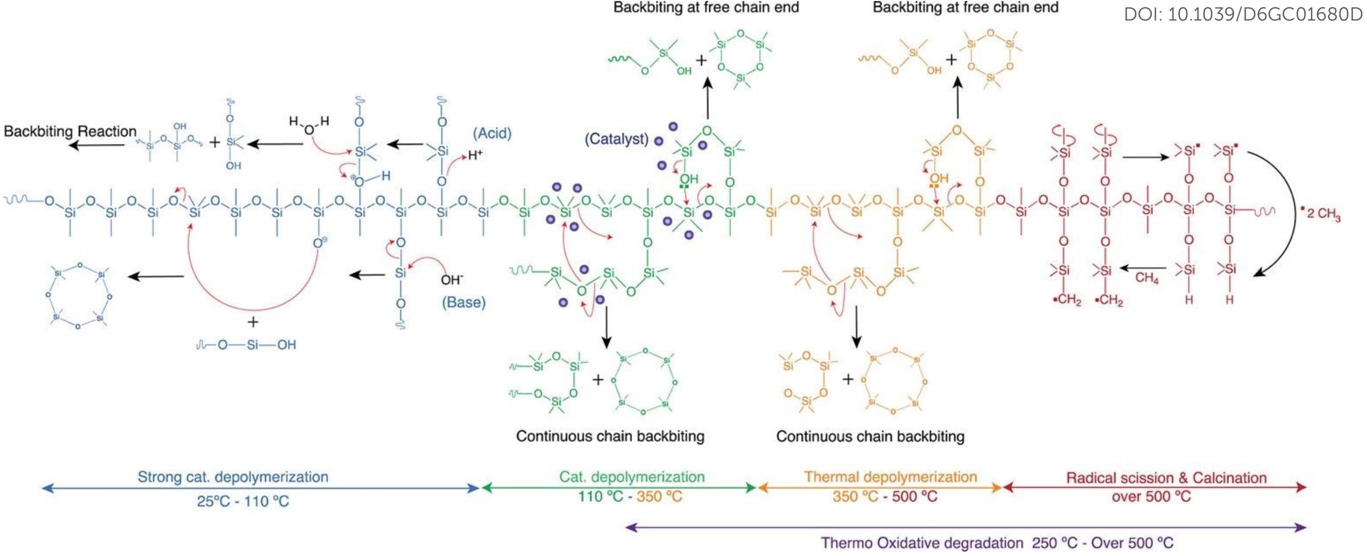

Figure 1. Main mechanistic pathways for the depolymerisation of silicones under different process conditions.[15] Reproduced with permission from Polymer International. © 2026 Society of Chemical Industry (SCI

2. Methodology

The LCA presented in this study was conducted in accordance with the ISO standards for life cycle assessment and follows the methodological framework defined in ISO 14040 and ISO 14044.[30] All synthetic routes were modelled in OpenLCA,[31] and prospective reaction modelling was carried out using the scale-up methodology adapted from Piccinno et al.[32]

This study comprises two complementary assessments. The first evaluates the life cycle of a representative commercial RTV silicone sealant formulated from virgin raw materials using an acetoxy condensation-curing system. The second examines selected recycling routes designed to regenerate either dimethyldichlorosilane (DMCS) or cyclic siloxanes as intermediates suitable for reintroduction into PDMS production. Together, these analyses aim to pinpoint the major contributors to carbon emissions across the silicone sealant value chain and to assess how effectively different recycling strategies can mitigate these impacts.

Following ISO 14040, the functional unit (FU) is defined as a physical reference. For the assessment of commercial sealants, the FU corresponds to 1 kg of silicone sealant at gate. For the comparison of recycling technologies, the FU is 1 kg of PDMS raw material available for subsequent formulation.

2.1 System Description

The system boundaries for the LCA of virgin silicone sealant are defined as cradle-to-gate, reflecting the broad range of application-specific conditions during the use phase. Because formulations vary across use cases and commercial products, a representative formulation was selected.[33] In addition to hydroxy-terminated PDMS and methyl-terminated PDMS as plasticizers, an acetoxy crosslinking system catalyzed by a tin compound is employed. A di-tert-butoxy-diacetoxysilane adhesion promoter and pyrogenic silica reinforcing filler are also included. The detailed composition is shown in Figure 2. The resulting life cycle inventory (LCI) of virgin RTV silicone production comprises six components:

PDMS-OH and PDMS-CH$_3$: The synthesis of PDMS with methyl or hydroxy end groups from fossil resources includes: (i) carbothermal reduction of quartz to silicon metal, (ii) grinding, (iii) the Müller–Rochow process for converting silicon metal and methyl chloride into methylchlorosilanes, (iv) distillation, (v) hydrolysis, (vi) ring-opening polymerization to PDMS, and (vii) purification.[34]

1) *Fumed Silica:* Silica production is modeled via the electric-arc pyrolysis of silicon tetrachloride in an oxygen–hydrogen flame at 3000 °C, yielding pyrogenic silica and hydrogen chloride.
2) *Dibutyltindiacetate (DBTA):* The tin-catalyst synthesis is represented through: a) disproportionation of tetra-n-butyltin with stannic chloride; b) hydrolysis to dibutyltin oxide (DBTO); and c) carboxylation with acetic acid.[35] All auxiliary chemicals, solvents, and energy inputs are included.
3) *Ethyltriacetoxysilane:* The production of this crosslinker is modeled via platinum-catalyzed hydrosilylation of trichlorosilane with ethylene, followed by acetoxylation with acetic anhydride under acetyl chloride cleavage.[36]
4) *Di-tert-butoxy-diacetoxysilane*: this additive is modeled as produced from silicon tetrachloride and acetic acid, followed by condensation with tert-butanol.[36]

Manufacturing of the final sealant product includes mixing, deaeration, incorporation of additives and catalyst, and filling; packaging is excluded.[34a] The life cycle impact assessment of silicone recycling processes is modeled as gate-to-gate, from silicone waste at plant to recycled PDMS, ensuring

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comparability between recycling technologies (Figure 2). Silicone waste collection and transportation are not considered in the model.

Thermal depolymerization is modeled according to the patent literature,[37] in which silicone elastomers are heated to 500 °C under a constant nitrogen flow. Cyclic siloxanes are distilled off, yielding three- to seven-membered cyclic dimethylsiloxanes with an efficiency of 93.9 %.

Acid-catalyzed depolymerization is modeled following the patented methodology:[16c] silicone elastomers are heated at 140 °C in 65 % aqueous sulfuric acid. After three hours and distillative purification, four- and five-membered dimethylsiloxane cycles are obtained in 89 % yield.

Base-catalyzed depolymerization follows the patented method,[20] heating silicone elastomers at 150 °C in 45 % aqueous potassium hydroxide. After 3.5 hours and purification, the yield of cyclic dimethylsiloxanes reaches 98 %.

Fluoride-catalyzed depolymerization is modeled according to the patented procedure,[26] in which silicone elastomers are stirred for 24 hours in a TBAF–tetrahydrofuran solution. After quenching with calcium chloride and filtration, the yield of cyclic dimethylsiloxanes is 93.3 %.

Metal catalyzed halogen-cleavage depolymerization:[25] silicone elastomers are heated at 40 °C in a 1 M boron trichloride/dichloromethane solution with catalytic gallium trichloride for 30 minutes. Distillation affords 99 % dimethylchlorosilane, which is then hydrolyzed in a 50 % water/dioxane mixture to give cyclic dimethylsiloxanes and hydrogen chloride.[38]

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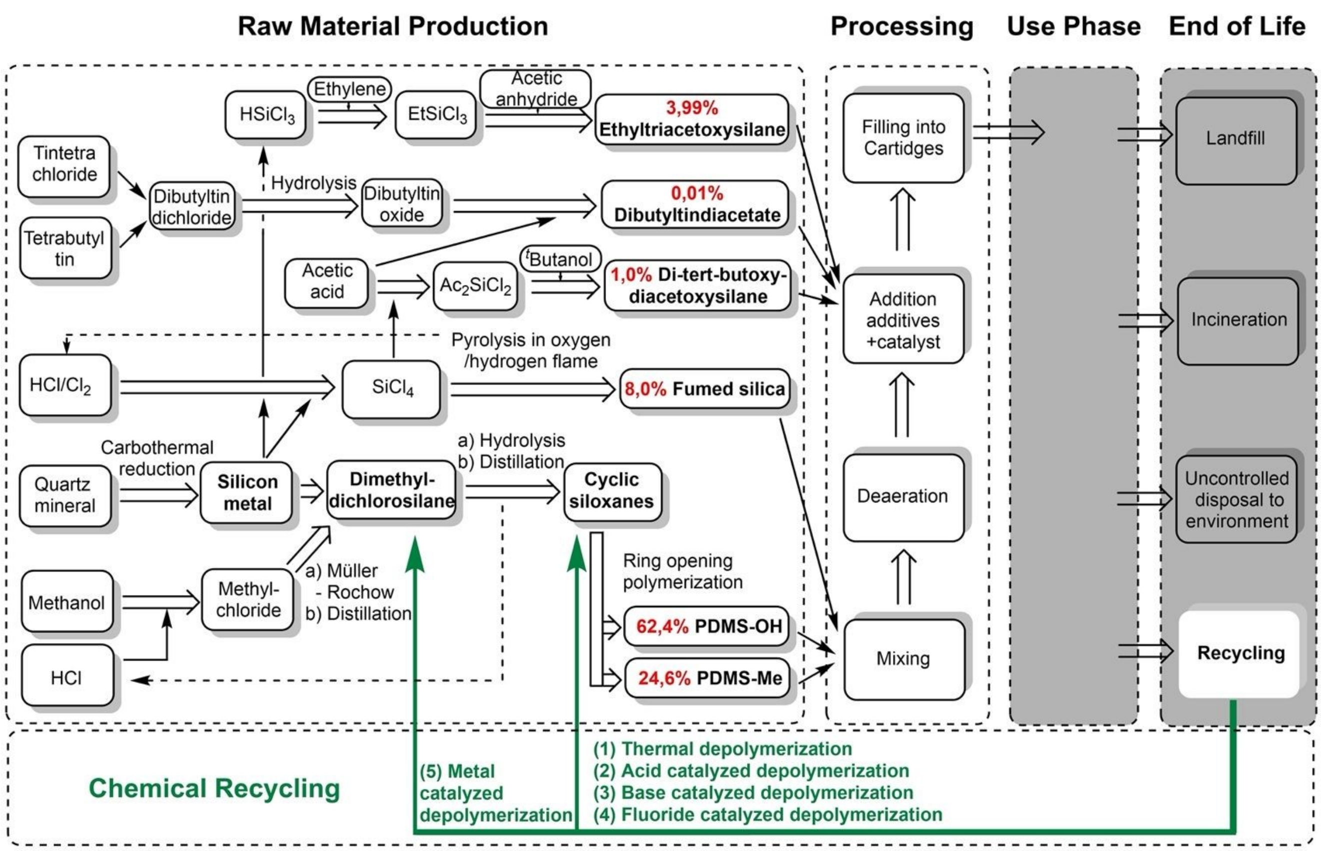

Figure 2. Process flowsheet and system boundaries for virgin and recycled RTV-1 silicone sealants, covering fossil-based raw-material synthesis and five recycling routes: (1) thermal; (2) acid-catalyzed; (3) base-catalyzed; (4) fluoride-catalyzed depolymerization to cyclic siloxanes; and (5) metal/halide-catalyzed depolymerization (BCl_3, $GaCl_3$) to DMCS

2.2 Data Collection

Data for the LCA were obtained from scale-up calculations, literature sources, databases, and proxy processes. These data are organized into several categories based on their relevance and quality.

Secondary data: Extrapolated literature and patent information were used to model the industrial-scale production of chemicals. Most literature data originated from gram- to kilogram-scale experiments. Secondary data for basic chemicals and auxiliary processes were sourced from the PEF 3.1 and Ecoinvent 3.7.1 databases. When specific chemicals were unavailable in these databases and used only in small amounts (below 0.5 %), suitable proxy chemicals were selected. These substitutes provide equivalent functions or share similar production pathways. Chemicals present in negligible quantities were excluded using a 0.01 % cut-off rule, as their contributions to overall impacts are considered insignificant.

2.3 Environmental Impact Assessment

Environmental impacts were calculated using the Environmental Footprint 3.0 method at the mid-point level, as developed by the European Commission. The life cycle impact

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assessment (LCIA) applies the standard PEF weighting and normalization factors. The method encompasses all major environmental impact categories.[39]

3. Results and Discussion

3.1 Silicone Production

The environmental impacts of the cradle-to-gate production of commercial RTV-1 silicones were evaluated across four impact categories, using a functional unit of 1 kg of silicone sealant. The categories include:

- Climate change (carbon footprint): a measure of the potential global warming impact associated with emissions of greenhouse gases such as CO_2, nitrogen oxides, and methane. Cumulative emissions are expressed as kg CO_2 equivalents using PEF weighting and normalization factors;
- Cumulative energy demand (CED): the total primary energy required throughout the supply chain, from raw material extraction and transport to manufacturing and production, reported in MJ;
- Resource use: the depletion of non-renewable mineral and metal resources, expressed as kg Sb equivalents, reflecting their reduced availability for future generations;
- Water use: the quantity of water consumed, expressed as m^3 deprived.

The silicone sealant formulation and relative contributions to these four impact categories are illustrated in Figure 3, and absolute values for all categories are provided in Table S1 (Supporting Information). The contribution patterns are consistent across all impact categories. PDMS components dominate the environmental burden, accounting for 82-89 % of the total impact, largely due to their high proportion in commercial formulations (87 %). Fumed silica also contributes disproportionately, particularly to climate change and CED, because of the energy-intensive production of silicon-based precursors and the flame pyrolysis process.

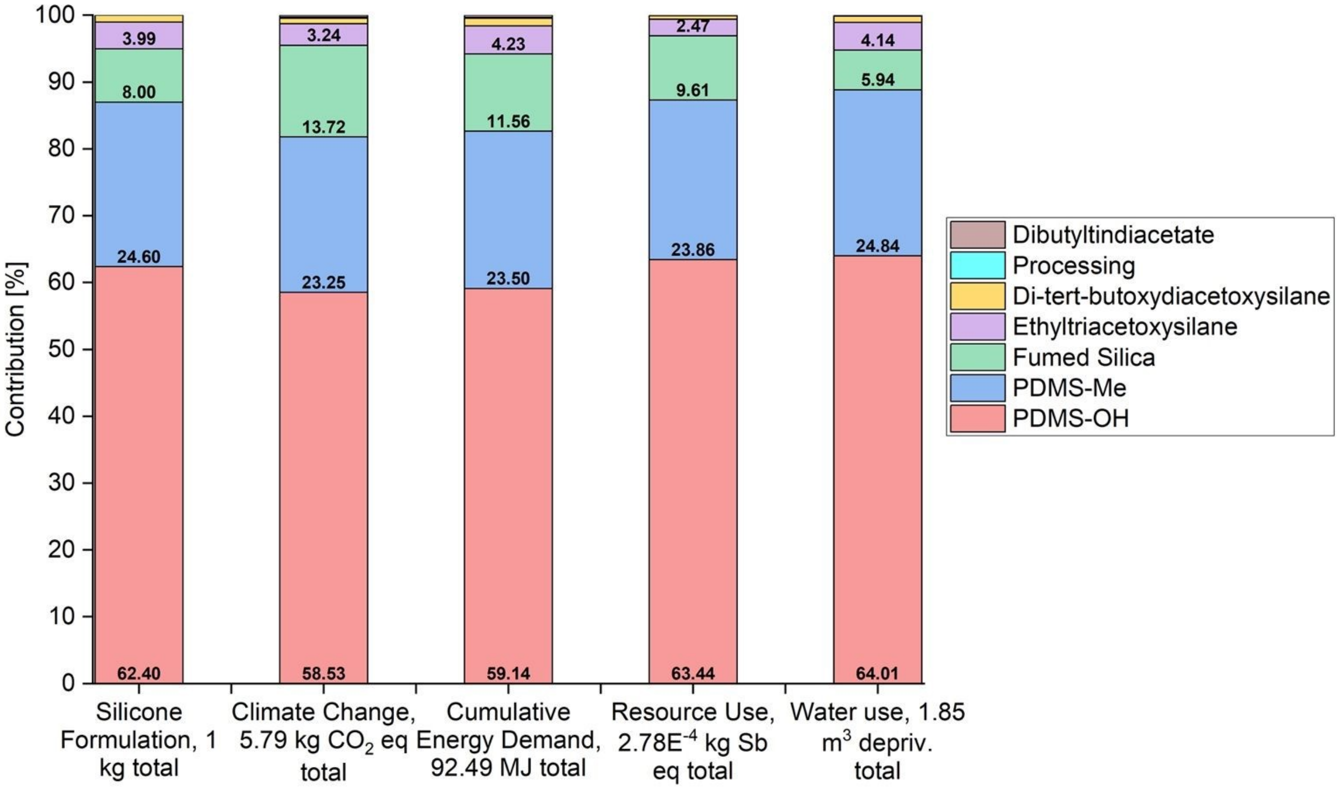

Figure 3. Percentage contributions of formulation components to cradle-to-gate environmental impacts: Silicone formulation composition, Climate change (5.79 kg CO_2 eq), Cumulative energy demand (92.49 MJ), Resource use (2.78×10^{-4} kg Sb eq), and Water use (1.85 m^3). Values <2 % are omitted

In contrast, the contributions of the adhesion promoter, catalyst, and processing steps are minimal. This is due to their low quantities in the formulation and the relatively low energy and auxiliary material demands of processing. The total climate change impact of 5.79 kg CO_2 eq. per FU is therefore primarily driven by PDMS and fumed silica. To account for variations in silicone sealant formulations and to further analyze the sources of environmental impact, the environmental profile of each individual component is presented in Figure 4.

When comparing the normalized impacts of each component, the contributions of PDMS and the reactive silanes fall within a range of 4.46 to 5.47 kg CO_2 equivalents per kilogram of raw material. These impacts arise primarily from silicon metal production, accounting for 26 % for di-tert-butoxydiacetoxysilane, 29 % for ethyltriacetoxysilane, and 60 % for PDMS, and increase proportionally with the silicon content of each substance. The second-largest contributions stem from reactants and auxiliary chemicals: methanol and HCl for PDMS

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(13 %), acetic acid and tert-butanol for di-tert-butoxydiacetoxysilane (63 %), acetic anhydride for ethyltriacetoxysilane (62 %), as well as energy consumption across all processes.

These results align with data from Zhao et al reporting 8.19 kg CO_2 eq. per kilogram of DMCS produced in China, highlighting the drastic impact of chlorosilanes as precursors representing the highest CO_2 eq. per kg raw material across the entire value chain.[34c] Furthermore, the impact of production location and the corresponding energy mix has to be emphasized. The direct impact of the choice of energy carrier on the environmental impact of an entire process is further discussed below.

Fumed silica exhibits a notably higher environmental burden, doubling the climate change impact and increasing CED by approximately 50 % relative to other silicon-based materials. This is attributable partly to its high silicon content (~46 %), which accounts for 58 % of its climate change impact. Additional contributions come from the energy-intensive flame pyrolysis of silicon tetrachloride at 3000 °C, responsible for an additional 18 % of the total impact.

DBTA stands out due to its comparatively large CED and climate change contributions per kg DBTA. Tin tetrachloride is the principal emission driver, contributing 52 % of DBTA's total impact. This is largely because its production involves high-temperature carbothermal reduction of tin oxides, releasing stoichiometric amounts of CO_2, followed by tin chlorination. Nevertheless, because DBTA is used only in very small quantities as a catalyst in silicone sealant formulations, its overall contribution to the product-level environmental impacts is negligible.

Detailed process results and total environmental impacts are provided in Table S2 (Supporting Information)

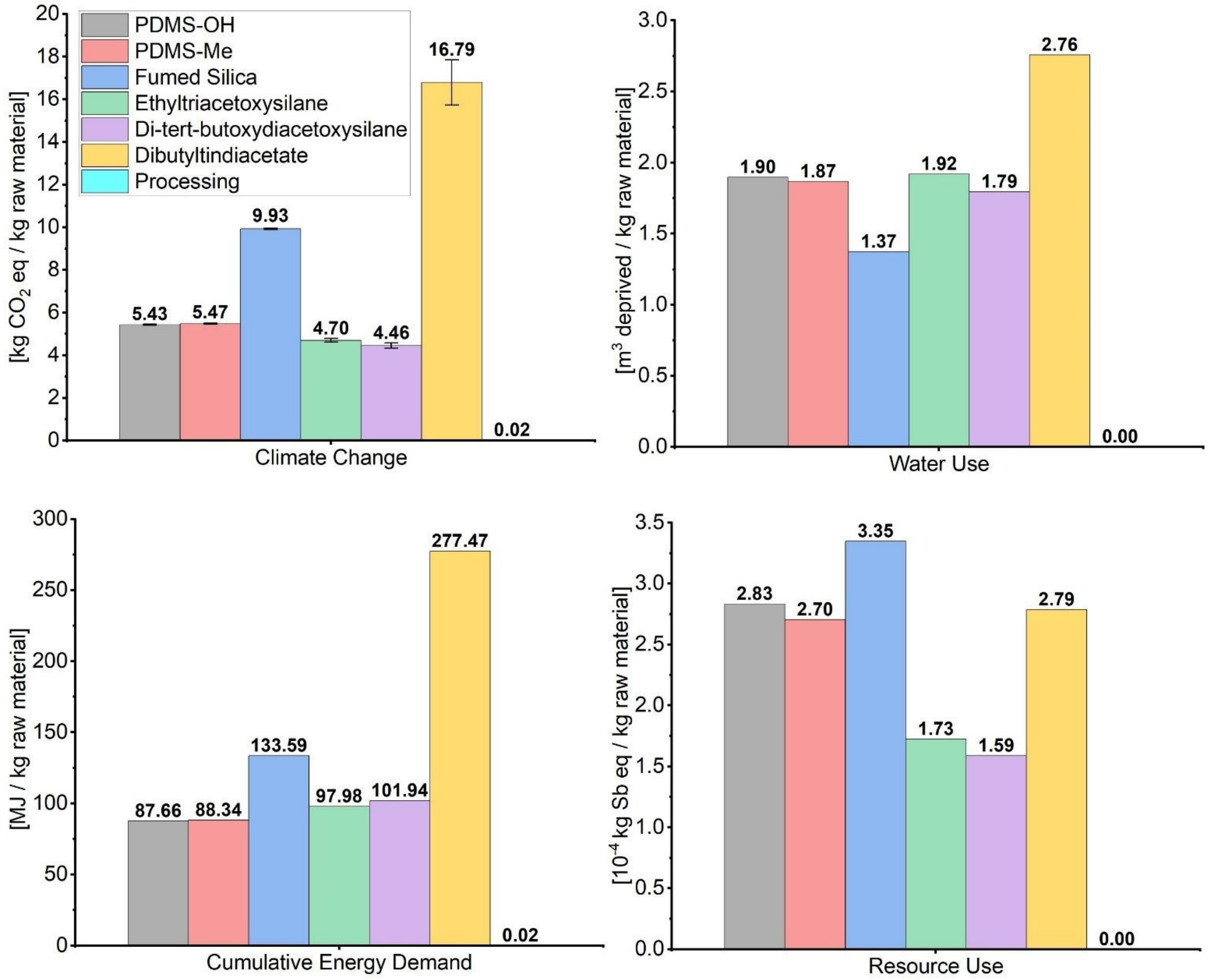

Figure 4. Total impacts per kilogram of virgin raw materials and processing for four categories: climate change, water use, cumulative energy demand, and resource use. Processing corresponds to producing 1 kg of silicone sealant with the specified formulation

3.2 Silicone Recycling

To reduce the environmental impacts of silicone sealants, the major emission drivers must be minimized, replaced, or recycled. As PDMS accounts for more than 80 % of the total

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environmental burden, five silicone recycling processes are compared. The focus lies on GHG emissions and the regeneration of PDMS suitable for reintegration into the sealant value chain. The selected recycling routes represent both established industrial practices and promising technologies emerging from academic research. These processes (see Section 2.1 and Figures 1 and 2) recover methylsiloxane cycles from post-use silicones via: high-temperature thermal depolymerization (1); low-temperature sulfuric acid–catalyzed depolymerization (2); low-temperature potassium hydroxide–catalyzed depolymerization (3); low-temperature TBAF-catalyzed depolymerization (4). In addition, one metal-halide depolymerization route is included, namely depolymerization using stoichiometric boron trichloride in the presence of gallium trichloride as catalyst (5). The latter method recovers DMCS for reintegration one step earlier in the value chain, prior to hydrolysis to generate methylsiloxane cycles,

All process metrics were scaled to an industrial capacity of 1000 kg based on the reported patent data. Processes (1)-(3) originate from kilogram-scale protocols and may allow moderate optimization; any distortions introduced by scaling are largely addressed within the applied scale-up framework. In this context, *moderate optimization* encompasses typical improvements associated with the transition from pilot- to industrial-scale operation, such as higher yields, lower solvent-to-product ratios, enhanced reagent efficiency, and heat recovery. Although these factors are approximated within the applied scale-up methodology, further optimization beyond the scope of the present study may be realized under industrial conditions. Processes (4) and (5), however, were reported only on gram scale and are therefore more susceptible to scale-related uncertainties. This is relevant regarding solvent volumes and energy requirements, which may deviate more substantially from industrial conditions than the scale-up framework can fully account for. Furthermore, no solvent recycling is assumed for any of the processes. Moreover, to effectively focus on the nature of the depolymerisation process, the PDMS model does not contain additives or fillers, which are challenging to recover in practice.

These uncertainties, as well as the influence of energy sources and solvent management, are examined in the sensitivity and uncertainty analyses presented in the following sections.

For comparability across recycling routes and with virgin PDMS, PDMS-OH is used as the functional unit. DMCS obtained from process (5) is hydrolyzed to dimethylsiloxane cycles, and all recovered cycles from the five processes are polymerized under identical conditions via potassium hydroxide-catalyzed ring-opening polymerization to yield usable PDMS. The resulting GHG emissions and CED values, expressed as totals based on process metrics and benchmarked against virgin PDMS, are shown in Figure 5. The impact of the reaction temperature, time, yield and amount of solvent used in each recycling process is summarised in the supporting information (Figure S1).

Recycling processes (1)-(4) reduce total GHG emissions associated with PDMS production by 28-66 %, with the base-catalyzed depolymerization route achieving the largest reduction. Across all processes, GHG emissions are dominated by thermal energy demand and the subsequent ring-opening polymerization step, which is constant for all routes. Differences among the first three processes primarily arise from yield, reaction temperature, and reaction time; of these factors, temperature has the largest influence, as reaction times are similar at approximately 3 hours.

Even though base-catalyzed recycling requires a slightly higher reaction temperature (10 °C more) and a longer reaction time (30 min more) than the acid-catalyzed route, its overall thermal energy demand is nevertheless lower. This results from the higher yield of the base-catalyzed process (98 %) compared to the acid-catalyzed process (89 %), which compensates for the additional heat input by reducing efficiency losses.

Thermal recycling also achieves more than a 50 % reduction in both GHG emissions and CED relative to virgin PDMS, despite its higher reaction temperature. This is largely because downstream purification is unnecessary and high-purity cyclic siloxanes are directly recovered. It is worth noting that, when compared with the energy-intensive stages of virgin PDMS production, such as the carbothermal reduction of quartz at 2000 °C or the Müller-Rochow process at 370 °C, thermal depolymerization at 500 °C remains energy-competitive.

In contrast, low-temperature routes can still show elevated energy demand, as illustrated by the TBAF process (4). Here, the substantial quantity of THF required leads to high energy consumption during distillative recovery of methylsiloxane cycles. Consequently, both the direct environmental burden of the solvent and the indirect burden through increased distillation energy reduce the overall impact-reduction potential. In the reported TBAF process, these combined solvent effects account for 70 % of total GHG emissions and 72 % of CED.

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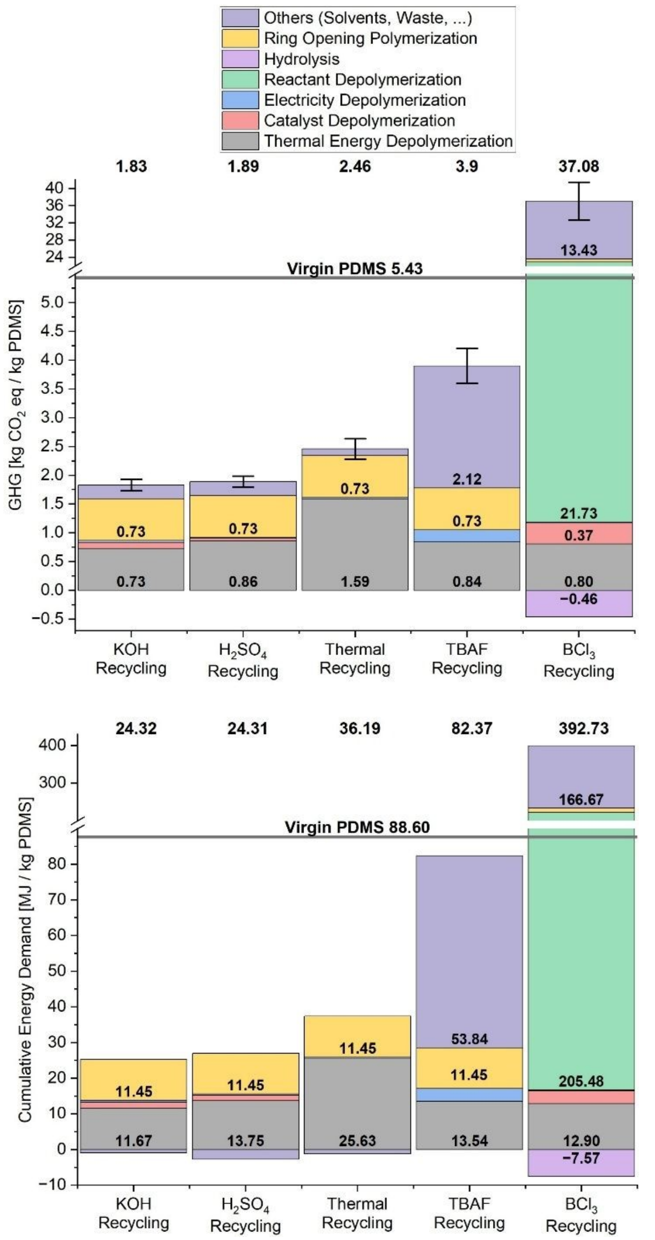

Figure 5. Climate change (GHG) and CED impacts of virgin PDMS and PDMS recovered via five recycling routes: KOH, H_2SO_4, thermal, TBAF, and BCl_3 depolymerization. Total values are shown above each bar; sub-process contributions appear below each sub-bar.

A similar trend appears when comparing the TBAF process with the other low-temperature route: metal-halide-catalyzed depolymerization to DMCS using boron trichloride (5). Here, large volumes of dichloromethane contribute substantially to direct environmental impacts and elevate energy demand during purification. In addition, the use of stoichiometric reactants and the step back to DMCS in the value chain further diminish the environmental benefits. Boron trichloride alone is sufficient to offset any potential emission savings compared with virgin PDMS, despite the low reaction temperature, short reaction time, and excellent yield (99 %) of this process. A summary of experimental variables impacting the thermal energy demand and consecutive environmental impact is given in the supporting information (Figure S1).

Although solvent recycling could mitigate some impacts, stoichiometric reactants inherently introduce low scale-up uncertainty and cannot be significantly reduced. Recovering boron trioxide from the reaction mixture is possible, but regenerating boron trichloride requires isolation, purification, and chlorination, releasing stoichiometric carbon monoxide and generating substantial additional environmental burdens. For all recycling processes examined, contributions from catalysts, electricity, waste treatment, and auxiliary materials are negligible due to their low usage volumes.

When recycled PDMS is incorporated into silicone sealant formulations, the overall environmental impact can be reduced, depending on the recycling route employed. The green-house gas emissions associated with producing 1 kg of silicone sealant at varying fractions of recycled material are shown in Figure 6.

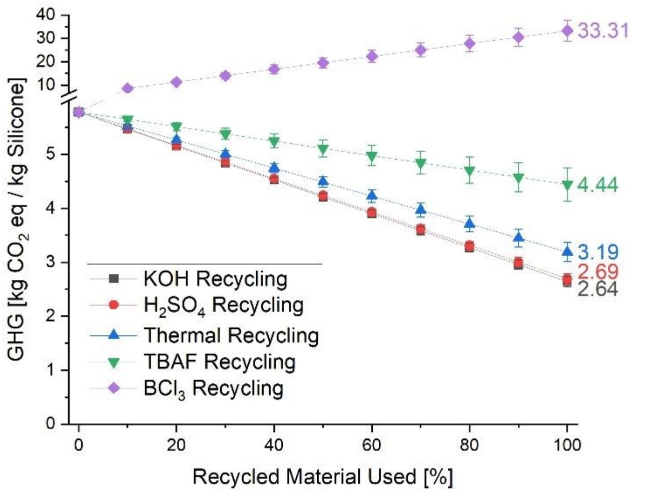

Figure 6. Climate change impact (as overall GHG emissions) of 1 kg of silicone sealant with 0-100 % substitution of virgin PDMS by recycled PDMS from the evaluated recycling routes.

The introduction of recycled PDMS into the value chain can significantly reduce overall GHG emissions, by up to 55 % in the best-case scenario, achieved with potassium hydroxide (KOH)-catalyzed recycling and 100 % substitution of virgin PDMS in the formulation. Under these conditions, total GHG emissions decrease from 5.43 kg CO_2 eq. to 2.64 kg CO_2 eq.

Across all recycling routes except the BCl_3 process, GHG savings are obtained regardless of the percentage of recycled PDMS used. Notably, because the recycled PDMS exhibits high purity and a controlled chain length, substitution at high levels does not present significant formulation challenges and is technically feasible at industrial scale. The effectiveness of recycling also depends on the PDMS content in the original silicone formulation and can therefore vary with the composition of the waste stream. In the formulation assessed here, which contains approximately 87 % PDMS, a favorable best-case scenario is achieved, and the GHG reduction potential scales linearly with the PDMS fraction. Conversely, the amount of silicone scrap required to produce 1 kg of recycled PDMS increases as the PDMS content decreases, for example, due to higher filler or extender levels. Similarly, differences in process yields affect both related emissions and the mass of scrap required, ranging from 1.19 to 1.61 kg of silicone waste per kilogram of recovered PDMS, depending on the process. When larger scrap quantities are needed to obtain the same amount of recycled PDMS, the environmental burdens associated with waste collection, purification, and transport, which are not included in this study, will also increase. These additional requirements may raise costs and challenge the economic feasibility of certain recycling routes.

3.3 Uncertainty Analysis

The primary source of uncertainty arises from systematic effects introduced by the scale-up methodology and by the underlying model development. To quantify the cumulative uncertainty in the calculated environmental impacts, a Monte Carlo analysis was performed. A log-normal distribution of emissions was assumed, and all input parameters were varied according to uncertainty factors derived from technology readiness and data quality, as defined by a pedigree matrix. Based on 1000 iterations and a 95 % confidence interval, the standard deviation of impacts for raw materials and silicone sealants ranges from ±0.3 % for processes with high-quality, well-documented data (e.g., virgin PDMS and fumed silica) to ±13.1 % for production routes requiring multi-level modeling from literature sources and databases. Within this framework, the reported environmental impact values can be considered reasonably reliable. Detailed Monte Carlo results are provided in the Supporting Information (Table S3).

3.4 Sensitivity Analysis

In the previously discussed cases, the thermal energy required for the recycling processes was assumed to be sourced from natural gas representative of the average EU technology mix. Solvent volumes were estimated using the scale-up framework and reduced by 20 %, following common recommendations for conservative efficiency improvements at larger scale. Solvent recycling from distillative purification was not considered in the base case but can substantially reduce GHG emissions for solvent-intensive processes. To evaluate the influence of these factors during scale-up, a sensitivity analysis was conducted for all recycling routes.

Effect of thermal energy source: The environmental impact of thermal energy, one of the major emission drivers, is strongly dependent on the energy carrier and production technology used during depolymerization, hydrolysis, and ring-opening polymerization (ROP). Natural gas remains the most important energy carrier for the chemical industry in Europe (0.070 kg CO_2 eq./MJ), whereas hard coal still plays a significant role, particularly in China, which accounts for 60 % of global silicon production. Therefore, the impacts of natural gas (0.072 kg CO_2 eq./MJ) and hard coal (0.108 kg CO_2 eq./MJ) as energy sources in China were compared with the EU reference, as well as the impact of biogas used within the European technology mix (0.029 kg CO_2 eq./MJ), representing renewable thermal energy. Resulting deviations for each recycling process are illustrated in Figure 7.

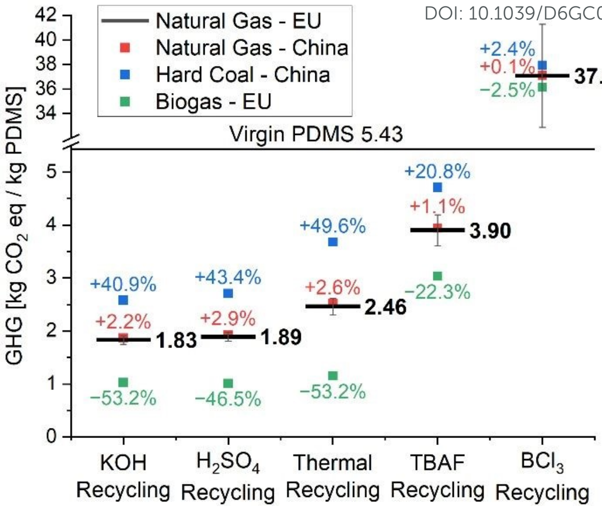

Figure 7. Climate change impact (as overall GHG emissions) of 1 kg of recycled PDMS across recycling routes using natural gas, hard coal, or biogas as the thermal energy source.

Shifting the energy source leads to increases of 0.1–2.9 % in GHG emissions when natural gas from China is used, 2.4–49.6 % when hard coal from China is used, and decreases of 2.5–53.2 % when EU biogas is applied. Thermal recycling was found to be the most sensitive to changes in energy sourcing, with climate change impacts decreasing by more than 53 % when using biogas and increasing by over 49 % when using hard coal. However, even under the most favorable conditions, acid- and base-catalyzed depolymerization remain the most efficient routes in terms of GHG reductions.

Within the scope of this study, variations in the energy carrier alone were insufficient to enable any recycling technology to achieve a climate impact equal to or lower than that of virgin PDMS; nevertheless, substantial emission savings can be lost (or gained) depending on the energy source. Importantly, selecting a low-carbon thermal energy source allows acid- or base-catalyzed recycling to achieve total GHG emissions of approximately 1 kg CO_2 eq. per kg PDMS, representing reductions of more than 80 % compared to virgin PDMS. The pronounced influence of geographic location and the origin of thermal energy underscores the importance of these factors when scaling recycling technologies, purchasing recycled PDMS, comparing products on the market, or developing corporate sustainability strategies

Effect of solvent recycling: Another key factor influencing the performance of the recycling processes is the use of organic solvents, particularly in the TBAF and BCl_3 depolymerization routes. In both cases, the solvents are recovered at high purity during the distillative purification step and can therefore be returned to the reaction as the solvent medium. In contrast, the acid-, base-, and thermal-recycling processes do not employ organic solvents; distillation yields only water as a separable stream, which can be reused. The influence of solvent reuse on GHG emissions, expressed relative to the percentage of solvent recovered, is shown in Figure 8.

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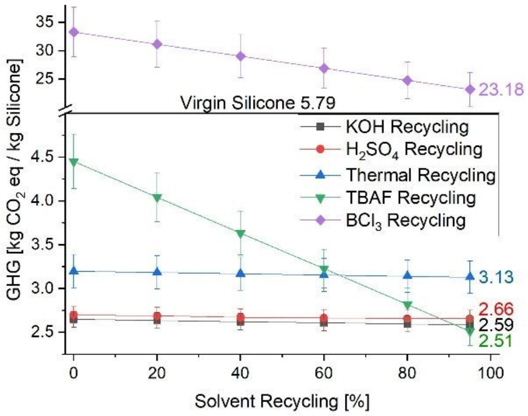

Figure 8. Climate change impact (as overall GHG emissions) of producing 1 kg of RTV silicone using 100 % recycled PDMS, shown for different recycling processes and varying solvent-recycling efficiencies.

As expected, solvent recycling has a negligible effect on the acid-, base-, and thermal-recycling processes due to the absence of organic solvents in these systems. In the boron trichloride process, however, substantial GHG reductions are achieved (up to roughly 10 kg CO_2 eq. at 95 % solvent-recycling efficiency), driven primarily by the recovery of dichloromethane (3.50 kg CO_2 eq./kg dichloromethane). Nevertheless, because the impact of boron trichloride itself remains unchanged, this process continues to be environmentally unfavorable compared with virgin PDMS production.

TBAF-catalyzed recycling also benefits significantly from solvent recovery during the purification step, with potential GHG reductions of up to 43 %. This improvement is largely attributable to the substantial solvent volume and the high footprint of tetrahydrofuran (5.73 kg CO_2 eq./kg THF). Because solvents are the dominant emission source in the TBAF process, solvent recycling brings its total GHG emissions into the same range as those of acid- and base-catalyzed depolymerization. In fact, at a 95 % recycling rate, TBAF depolymerization becomes the most environmentally efficient route due to the additional advantage of low thermal energy demand.

4. Conclusion

In this study, an LCA and a prospective LCA were jointly conducted to evaluate the environmental impacts of silicone elastomers and their chemical recycling into either cyclic dimethylsiloxanes or DMCS. Using OpenLCA, the GHG emissions of virgin silicone elastomers were quantified as 5.79 kg CO_2 eq. per kilogram of product, with PDMS identified as the dominant contributor (82 %) in a representative formulation containing 87 % PDMS. The prospective LCA of recycling routes revealed strong dependencies of environmental performance on reaction temperature, purification requirements, solvent management, and the use of stoichiometric reactants.

Under standard assumptions, KOH-catalyzed depolymerization exhibited the lowest GHG emissions among the assessed recycling processes, producing PDMS with an impact of 1.83 kg CO_2 eq. per kilogram. Incorporation of recycled PDMS into silicone elastomer formulations can therefore reduce overall emissions by up to 55 %. Sensitivity analyses further demonstrated that all processes are highly responsive to changes in thermal energy sources, while the TBAF and boron trichloride routes are additionally very sensitive to solvent recycling rates. Organic solvents were shown to contribute substantially to environmental burdens; however, their impacts can be markedly reduced when solvents recovered during distillative purification are reused. At solvent recycling efficiencies above 90 %, the TBAF-based process achieves the lowest GHG emissions of all routes investigated. In contrast, the boron trichloride process highlights the disadvantages associated with stoichiometric reactants and with recycling schemes that return intermediates to earlier, less energy-efficient stages of the value chain.

While each recycling route has been analyzed individually, it is equally important to interpret the results across scales from molecular mechanisms to process performance and life-cycle outcomes. The depolymerisation chemistry under scrutiny has been demonstrated to influence the energy and material efficiency observed at process scale. For instance, the elevated siloxane yield and diminished by product formation in base catalyzed depolymerisation have been shown to directly reduce the thermal energy requirement and thus the overall greenhouse gas emissions. Conversely, solvent intensive or stoichiometric halide routes impose intrinsic limitations that propagate upward, increasing embodied energy and offsetting potential savings. The mechanistic characteristics under scrutiny are shown to translate into distinguishable environmental profiles when scaled to ton-scale. Consequently, the variability observed at the reaction level encompassing yield, selectivity, and solvent dependency constitutes the predominant source of uncertainty in the macro scale sustainability assessment.

Overall, given the increasing global demand for silicone elastomers, reducing their environmental footprint is essential. The integration of reaction engineering principles with LCA modelling provides a more cohesive understanding of how molecular design choices influence system level circularity and environmental performance. This study demonstrates that several chemical recycling pathways offer meaningful emission-reduction potential and can serve as an important pillar in advancing a more circular and sustainable silicone industry.

Author contributions

Malte Kunz: Conceptualization, Methodology, Investigation, Writing - Original Draft **Shamna Salahudeen**: Resources, Writing - Review & Editing **Esteban Mejía:** Conceptualization, Supervision, Writing - Review & Editing.

Conflicts of interest

There are no conflicts to declare.

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Data availability

The supporting data has been provided as part of the Supplementary information.

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Data availability

The supporting data has been provided as part of the Supplementary information.