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Comparative Life Cycle Assessment of Recyclable Polyhydroxyurethanes Synthesized from Five- and Six-Membered Carbonates

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Abstract: Polyhydroxyurethanes (PHUs) synthesized from cyclic carbonates are promising alternatives to conventional polyurethanes due to their advantageous isocyanate-free synthesis and reprocessability characteristics. While many studies focus on PHUs derived from five-membered cyclic carbonates (5CCs) for more sustainable synthesis routes, PHUs from six-membered cyclic carbonates (6CCs) exhibit enhanced reactivity towards amines. Their reprocessability is facilitated by the presence of hydroxyl groups along the polymer chain, enabling transcarbamoylation reactions. However, since non-catalyzed transcarbamoylation is typically a sluggish reaction, catalysts are often required to enhance network reprocessability. This study presents a life cycle assessment (LCA) of PHU-5CC and PHU-6CC syntheses, with catalysts, for recycling applications targeting end-of-life scenarios. Environmental impact categories, including climate change, particulate matter, fossil resource depletion, mineral and metal resource use and freshwater eutrophication, were evaluated. Sensitivity analyses were also conducted to assess key variables. Our results indicate that PHUs from 6CCs show a higher environmental footprint due to their solvent-intensive synthesis process. Despite the increased reactivity and shorter reaction times associated with the 6CC monomer, these benefits do not fully offset the environmental impacts of the synthesis process. In conclusion, this study highlights potential improvements for future PHU synthesis, such as solvent-free processes, metal-free catalysts and optimized reaction monitoring.

Keywords: bio-based polymers; life cycle assessment; polyhydroxyurethanes; non-isocyanate polyurethanes



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1. Introduction

Polyurethanes (PUs) are currently the sixth most produced polymer in the world, with annual production of 20 million tons [1,2]. They are an integral part of our daily lives, thanks to their low cost and excellent mechanical properties, chemical resistance and thermal stability. PUs are mainly used as flexible and rigid foams (65%), and also coatings (13%), elastomers (12%), adhesives (7%) and in the medical sector (3%) [2]. Although their properties are attractive, thermoset polyurethanes—which account for 60% of

PU, or over 12 million tons per year—have a permanent covalently cross-linked structure that makes them hard to recycle and reprocess [1,3–7]. The recycling of thermosets is a necessary challenge to avoid landfilling, which is currently the most widely used method for managing the end-of-life of PU-based products. Several recycling methods already exist, such as thermal treatments (energy recovery), mechanical recycling or chemical recycling. However, these methods are complex, energy-intensive and often require heavy necessary infrastructure for effective, large-scale recycling [8]. Chemical recycling involves the use of solvents, which can be toxic, and catalysts are often needed. Additionally, hazardous gases (e.g., carbon dioxide and monoxide, hydrogen, methane, etc) can be released during thermal treatments [9,10]. Hence, the disposal of PU waste presents both environmental and financial challenges. In addition, PU synthesis involves the use of toxic isocyanate building blocks, which also causes environmental and health problems [11–13]. Consequently, designing sustainable and reprocessable PUs is an important goal.

In this context, polyhydroxyurethanes (PHUs), a type of non-isocyanate polyurethane (NIPU) synthesized from cyclic carbonates and amines, appear to address both issues. The chemistry of PHUs avoids the use of toxic isocyanates and involves the formation of additional primary or secondary hydroxyl groups in each repeating unit along the polymer chain [14]. These hydroxyl groups can allow a dynamic exchange with carbamate groups present in the network, a process known as transcarbamoylation reaction (Figure 1a). The presence of these groups confers dynamic properties to PHUs that enable them to be reprocessed or reshaped, and allows PHUs to be categorized as CANs (covalent adaptable networks) [15–17] and especially recognized as vitrimers in the literature [18]. CANs are a class of polymeric materials that can interestingly combine the properties of both thermosets and thermoplastics. These materials possess dynamic covalent networks that can be remodeled in response to various external stimuli, such as light irradiation [19], pH variations [20], or temperature [21]. Vitrimers are subtype of CANs with an associative mechanism [22] and exhibit a particular rheological viscoelastic behavior, as observed in inorganic vitreous silica.

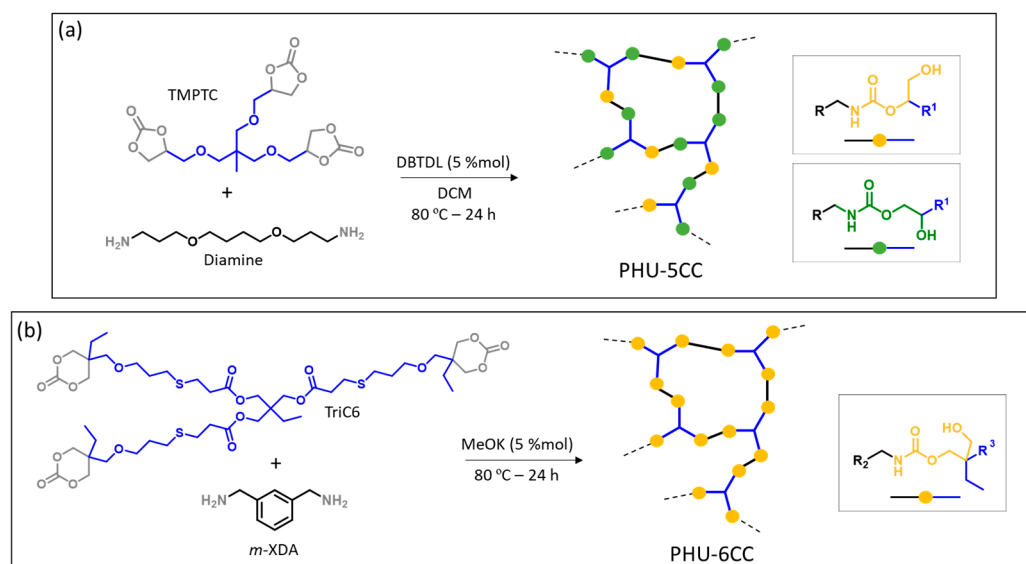


Figure 1. (a) Synthesis of PHU-5CC and (b) synthesis of PHU-6CC.

PHU-CANs derived from five-membered cyclic carbonates (5CCs) are the most extensively studied due to the fact that their synthesis is considered environmentally friendly, since 5CCs can be obtained from renewable raw materials among polyols [23], olefins [24], epoxy-based compounds and carbon dioxide [25–29]. However, 5CCs are not very reactive

towards amines [30]. The second type of carbonate used for PHU-CAN synthesis are six-membered carbonates (6CCs) [18,31–38]. Though being more reactive, 6CCs are more difficult to synthesize and require a multi-step synthesis. The most efficient synthesis requires the use of phosgene derivatives [30,31,34,39–43] and is therefore considered more harmful to the environment [44]. Some studies have focused on the use of carbon dioxide (CO₂) for their phosgene-free synthesis, but yields are low and several steps are needed. For instance, Liu et al. [35] synthesized a bifunctional 6CC with a 37% yield from CO₂ and isoeugenol. Miao et al. [37] also obtained a resveratrol-based tri(six-membered cyclic carbonate) with 46% total yield from multi-step synthesis using CO₂. Other phosgene-free syntheses exist with higher yields, but these require longer reaction times. For instance, Endo et al. [45–50] have developed and presented 6CC synthesis using di(trimethylolpropane) with diphenyl carbonate at 140 °C for 48 h with good yields ranging from 60 to 82%. Jehanno et al. [51] obtained different functionalized 6CC from depolymerized polymer wastes, showing another more sustainable alternative.

Although PHU-CANs can be produced without catalysts, non-catalyzed transcarbamoylation is relatively slow, even at high temperatures, limiting the potential for end-of-life reprocessing. In PHU-CANs derived from 5CCs, Chen et al. [33] and Hu et al. [24] introduced 4-dimethylaminopyridine (DMAP) as a catalyst into the PHU network to enhance its dynamic properties. Recently, our team [52] investigated the use of different catalysts and showed that dibutyltin dilaurate (DBTDL) was effective in promoting transcarbamoylation reaction within the network. For PHU-CANs from 6CCs, only DBTDL was tested by Saeed et al. [38] in the reprocessing of a PHU nanocomposite or internal catalyst, though the use of tertiary amines was studied [18,31].

Identifying key aspects of a more-sustainable PHU-CAN synthesis to minimize environmental impact is a complex, data-intensive task. Mundo et al. [29] employed the *E-factor* (relating the mass of waste generated by the process to the mass of product) and toxicity metrics to promote greener synthesis approaches within the context of 5CC production. Life cycle assessment (LCA) also serves as an ideal and effective tool for comparing the environmental impact of different production methods or systems [53,54]. There is currently only one article that deals with the LCA of a PHU. Hence, Liang et al. [55] showed that PHU from biomass which can be reprocessed after depolymerization can reduce greenhouse gas emissions and save fossil energy if the reprocessing conditions are optimized; they also identified water consumption in the synthesis and reprocessing of PHU as the most significant environmental impact. While not published as a peer-reviewed article, it is worth mentioning that Materia Nova's team also carried out LCAs involving PHU [56]. However, there is no comparison of the environmental impact of replacing 5CCs with more reactive 6CCs.

The present study is distinctive in its focus on environmental considerations, aiming to conduct an LCA comparing two different synthesis pathways for the production of PHU-CAN. To this end, we compared two PHU synthesis routes: one based on a 5CC and the other on a 6CC. The choice of trifunctional carbonates was based on efficient syntheses in laboratories, with a bio-based 5CC as opposed to a petro-based 6CC. At this stage, syntheses of bio-based 6CCs are not included in this life cycle assessment due to their low yield and high number of reaction steps (more than two), which would have a higher environmental impact than their petro-based equivalent [35,37]. In the same comparative approach, an aliphatic amine is contrasted with an aromatic amine, while two different catalysts are also compared.

Both syntheses selected were conducted to gather all the necessary data, ensuring the reliability of our environmental impact assessment. The synthesis of PHU-5CC involves using a five-member bio-based carbonate in the presence of 4,9-dioxa-1,12-dodecanediamine

(diamine) and dibutyltin dilaurate (DBTDL) as a catalyst. Conversely, the synthesis of PHU-6CC employs a six-member petro-based carbonate alongside m-xylylenediamine and potassium methoxide (MeOK) as the catalyst. These specific syntheses are not the most optimized, allowing us to identify sensitive points and potential avenues for improvement. The primary objective of this study is to determine the most sustainable method for producing PHUs, comparing 5CCs and 6CCs to reduce the overall environmental footprint of the materials, based on the assumption that both PHUs are isofunctional at equal mass. The originality of this work lies in its innovative LCA approach, applied to a PHU specifically designed for recyclability at the end of its life through the use of catalysts. Additionally, the *E-factors* for both syntheses were calculated to complement the LCA study, providing a more comprehensive evaluation of their environmental performance.

2. Methods

2.1. Definitions and System Boundaries

As mentioned above, LCA is a precious environmental evaluation tool that enables the environmental impact of two production methods or systems to be compared [53,54]. LCA is based on international standards, ISO 14040 and 14044 [57]. The ISO 14040 standard defines the procedure for performing an LCA through four stages: study goals, life cycle inventory (LCI), impact assessment and interpretation at each stage.

LCIs include obtaining relevant information or input/output data (resource extraction and pollutant emissions, etc.) generated on the system studied. Such data can be tedious to search for in the scientific literature, and can be very time-consuming to produce. The conclusions reached by LCAs are highly dependent on the reliability and quality of these data.

Life cycle impact assessment is the stage at which the potential environmental impacts related to the inventory data can be calculated. These impacts are divided into several categories to facilitate interpretation (Table 1). The International Life Cycle Data System (ILCD) Handbook [58], based on international standard ISO 14040/44, is a guide to guarantee the quality, consistency and interpretation of data and methods when writing an LCA within a European context. To facilitate and improve the interpretation of the scores obtained, this guide contains a summary of the recommended methods and their classifications for each impact category. Three levels have been determined: (I) recommended and satisfactory, (II) recommended but intermediate interpretability (the method needs some improvement) or (III) recommended but potentially interpretable (method to be applied with caution). The list of recommended methods was recently updated for the environmental footprint method [59] and is reproduced in Table 1, where all acronyms are given for each environmental indicator.

In order to perform an LCA, a functional unit (FU) has to be defined. FUs define what is studied in terms of objective, chosen application and function, and can serve as a basis for the comparison of systems. The FU chosen in this study was a 10 g sheet of PHU-CAN measuring 7.5 cm by 4 cm and 1.5 mm thick. These dimensions were based on the constraints of the lab-scale experimental work. It was assumed that such sheets from the two materials PHU-5CC and PHU-6CC could be used for the same application. A cradle-to-gate system boundary was used: from raw materials to the production of a 10 g sheet of PHU-CAN.

Table 1. Recommended methods and their classification for each impact category from Joint Researcher Centre (European Commission) [59].

Impact Category	Acronym	Recommended Methods	Method Classification
Climate change	CC	Bern model—Global Warming Potentials (GWOs) over a 100-year time horizon, IPCC	I
Ozone depletion	ODP	EDIP model based on the ODPs of the World Meteorological Organization (WMO) over an infinite time horizon	I
Particulate matter	PM	UNEP-recommended model	I
Ionizing radiation	IR	Human health effect model	II
Photochemical ozone formation	POF	LOTOS-EUROS as applied in ReCiPe	II
Acidification	AC	Accumulated Exceedance	II
Eutrophication, freshwater	FE	EUTREND model as implemented in ReCiPe	II
Eutrophication, marine	ME	EUTREND model as implemented in ReCiPe	II
Eutrophication, terrestrial	TE	Accumulated Exceedance	II
Water use	WAT	Available Water Remaining (AWARE)	III
Land use	LU	Soil quality index based on LANCA (EC-JRC)	III
Resource use, fossils	RES-f	CML 2002—Abiotic resource depletion, fossil fuels	III
Resource use, minerals and metals	RES-m	CML 2002—Abiotic resource depletion, ultimate reserves	III
Human toxicity, cancer	HT-c	USEtox 2.1 model	III
Human toxicity, non-cancer	HT-nc	USEtox 2.1 model	III
Ecotoxicity, freshwater	FWT	USEtox 2.1 model	III

2.2. LCA Methodology

The purpose of the LCA was to compare the environmental impacts of two syntheses for the laboratory-scale production of 10 g of PHU-CAN. At the moment, only lab-scale data are available. It should be noted that these often have a greater impact than commercial materials prepared using optimized methods at the industrial scale. A cradle-to-gate system boundary was used for LCA and was modeled using Simapro 9.6.0.1 with the Ecoinvent database 3.10 (cut-off version). The studied steps of the life cycle began with the production of the resources required for each synthesis (extraction, energy, oil, natural gas, etc.) and ended with the production of a 10 g PHU-CAN sheet, the functional unit. Calculations for each impact category were carried out using the “Environmental Footprint 3.1” method, as provided in Simapro 9.6. Detailed life cycle inventories are included in the Supplementary Information (SI).

2.3. Life Cycle Inventory LCI

The inventories for the syntheses of PHU-5CC and PHU-6CC were based on Ecoinvent 3.10 (Cut-off version) background data. For chemical molecules or processes not included in this database, approximations were made. In some cases, generic average dataset (for organic and inorganic chemicals) values were used; in other cases, a model was prepared for describing the production of the molecule based on information obtained from the scientific literature (similar LCAs, existing protocols in articles, patents, etc.),

from datasets for similar chemicals, or from former LCA projects carried out at Materia Nova [56]. For each modeled process, inventories are listed in the tables provided, including all necessary information for the reproduction of the models (Tables S1, S2, S4–S7).

2.4. Chemicals and Instrument

Trimethylolpropane triglycidyl carbonate (TMPTC) [60] and 2-ethyl-2-(((3-((5-ethyl-2-oxo-1,3-dioxan-5-yl)methoxy)propyl)thio)propanoyl)oxy) methyl)propane-1,3-diyl bis(3-((3-((5-ethyl-2-oxo-1,3-dioxan-5-yl)methoxy)propyl)thio)propanoate) (TriC6) [61] were prepared according to the literature. 4,9-Dioxa-1,12-dodecanediamine (99%), azobis isobutyronitrile (AIBN) (98%), dibutyltin dilaurate (DBTDL) (95%), ethyl chloroformate ($\geq 98\%$), hydrochloric acid (37%), magnesium sulfate ($\geq 99.5\%$), potassium methoxide (MeOK) (95%), *m*-xylylenediamine (*m*-XDA) (99%), tetrabutylammonium bromide (99%), trimethylolpropane triglycidyl ether (TMPTGE), trimethylolpropane tris(3-mercaptopropionate) (TMPTM) ($\geq 95\%$), trimethylolpropane allyl ether (TMPAE) (100%), trimethylolpropane tris(3-mercaptopropionate), trimethylamine ($\geq 99\%$) were purchased from Sigma Aldrich (Darmstadt Germany). Carbon dioxide (CO₂) was acquired from Air Liquide (France). Ethyl acetate, 1,4-dioxane, tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from VWR International S.A.S (Fontenay-sous-Bois, France). Both curing took place in a model 4122 hot press (Carver, Wabash, IN 46992-0298, USA).

2.5. PHU-CAN Synthesis

PHU-5CC was prepared from 10 g (1 eq. per carbonate function) of TMPTC, 5.71 g (1.01 eq. per amine function) of 4,9-dioxa-1,12-dodecanediamine (diamine) and 5 mol% relative to the carbonate functions of DBTDL at 80 °C over 24 h, conditions described in a previous paper [52] (Figure 1a). The trifunctional 5CC (TMPTC) reagent was synthesized according to the study of Coste et al. [60]. PHU-6CC was prepared from 7 g (1 eq per carbonate functions) of the trifunctional 6CC monomer TriC6, 1.4 g (1.01 eq. per amine function) of *m*-XDA and 5 mol% relative to the carbonate functions of MeOK at 80 °C over 24 h (Figure 1b). The synthesis of the TriC6 monomer was inspired by the tetrafunctional synthesis in the study of Coste et al. [61], where pentaerythritol tetrakis(3-mercaptopropionate) was replaced by trimethylolpropane tris(3-mercaptopropionate).

2.6. Energy Calculations for Organic Molecule Synthesis and for PHU-CAN Synthesis

Piccinno and coworkers [62] have described a procedure to evaluate the scaled-up chemical processes from the laboratory to industrial scale. In their work, it was possible to find equations to approximate the energy required for a chemical synthesis. To calculate the energy required to synthesize the monomers used here, the required heating energy Q_{react} (Equation (1)), the stirring energy E_{stir} (Equation (2)) and the energy required for solvent removal Q_{solvent} (Equation (3)) were calculated. The details of these equations as well as the characteristics of the reactor can be found in the studies of Piccinno et al. [62] and Muegge [63].

$$Q_{\text{react}} = \frac{Q_{\text{heat}} \cdot Q_{\text{loss}}}{\eta_{\text{heat}}} = \frac{C_p \cdot m_{\text{mix}} \cdot (T_r - T_0) + A \cdot \frac{k_a}{s} \cdot (T_r - T_{\text{out}}) \cdot t}{\eta_{\text{heat}}} \quad (1)$$

$$E_{\text{stir}} = \frac{N_p \cdot \rho_{\text{mix}} \cdot N^3 \cdot d^5 \cdot t}{\eta_{\text{stir}}} \quad (2)$$

$$Q_{\text{solvent}} = Q_{\text{boil}} + Q_{\text{evap}} = m_{\text{solvent}} \cdot C_p \cdot (T_{\text{boil}} - T_0) + m_{\text{solvent}} \cdot \Delta H_{\text{vap}} \quad (3)$$

These equations include the energy to reach the reaction temperature Q_{heat} , energy to compensate the heat loss Q_{loss} , energy needed to heat solvent to boiling point Q_{boil} , energy

required for evaporation Q_{evap} , efficiency of the heating device η_{heat} , solvent specific heat capacity C_p , mass of the reaction mixture m_{mix} , reaction temperature T_r , starting temperature T_0 , surface area of the reactor A , thermal conductivity of the insulation material k_a , thickness of the insulation s , temperature difference between the inside and outside of the reactor $T_r - T_{\text{out}}$, reaction time t , type N_p (dimensionless number) and diameter d of the impeller, rotational velocity of stirring N , density of the reaction mixture (ρ_{mix}), mass of the solvent to evaporate m_{solvent} , boiling temperature of the solvent T_{boil} and enthalpy of vaporization ΔH_{vap} .

The synthesis and processing of the two PHU-CANs took place at 80 °C for 24 h in a hot press. The electricity consumption over 24 h at 80 °C was recorded using a wattmeter, measuring 7.37 kWh. This measurement corresponded to a sample weighing approximately 231 g, estimated based on the surface area of the heating plates, which could accommodate a maximum sample size of 33.21 cm.

2.7. E-Factor Definition and Calculation

The *E-factor* (environmental factor) is a metric introduced by Roger Sheldon in the early 1990s [64] to assess the environmental impact of chemical processes. It is widely recognized as a tool for evaluating the potential environmental acceptability of a chemical synthesis. The *E-factor* is defined as the mass ratio of the waste produced to the desired product, and it is calculated using the following equation:

$$E - factor = \frac{\text{mass of waste}}{\text{mass of desired product}} = \frac{\text{mass of raw materials} - \text{mass of desired product}}{\text{mass of desired product}} \quad (4)$$

Solvent contribution to *E-factor* was calculated using the following equation:

$$E - factor(\text{solvent}) = \frac{\text{mass of solvent}}{\text{mass of raw materials}} \cdot E - factor \quad (5)$$

An ideal *E-factor* is zero, which would indicate a process with no waste generation. In reality, the higher the *E-factor*, the more waste is generated, implying a potentially greater environmental burden [65]. Thus, the *E-factor* provides valuable insight into the sustainability of a process, as it accounts not only for the efficiency of the reaction but also for the quantity of by-products and residual materials produced.

3. Results and Discussion

The purpose of this LCA study is to assess the environmental impacts associated with the use of different compounds in the synthesis of PHU-CANs, in order to identify the main levers for improvement.

This LCA study concerns the use of trifunctional bio-based and petro-based cyclic carbonates and allows us to evaluate different catalytic and diamine choices. To this end, we synthesized two types of PHUs. As shown in Figure 1a, PHU-5CC was synthesized from a bio-based five-member cyclic carbonate TMPTC, with 4,9-dioxa-1,12-dodecanediamine (diamine), a DBTDL catalyst and DCM solvent. These compounds and this protocol were selected since they have already been produced and studied by our team [52]. For the second synthesis (Figure 1b), a six-member petro-based cyclic carbonate (TriC6) was chosen for its well-known synthesis pathway in our laboratory [61], paired with the aromatic diamine *m*-XDA, known to improve mechanical properties. The effect of DBTDL on a 6CC-based network has been previously demonstrated [38]. Since DBTDL was selected for PHU-5CC, the alkali metal-based catalyst MeOK was used here to broaden the insights into catalyst choice for PHU networks. On the other hand, the synthesis of this PHU-6CC was homogeneous without the use of solvent.

The goal was not to precisely simulate hypothetical industrial conditions but to approach them while extending beyond lab-scale data. Given that only lab-scale data are available, the environmental impact is likely to be greater than if commercial compounds or more suitable processes were used. For example, the amount of solvent per gram of product used in laboratory reactions is significantly higher than that typically used in industrial settings. Additionally, in industry, solvents can often be regenerated after reactions through distillation or filtration, which is not feasible at the laboratory scale. Scaling up the processes would enhance the environmental analysis, making it more reflective of real-world scenarios. Consequently, a 20% reduction was applied to solvent use [62], and market data, including chemical transport and manufacturing, were incorporated. Moreover, for both PHU-CAN syntheses, a curing time of 24 h at 80 °C was selected to ensure a high conversion rate of the carbonate (below 90%); however, these conditions are neither optimized nor fully adapted.

3.1. PHU-5CC-Inventories

Figure 2 shows the various steps in the production of PHU-5CC. First, the monomer TMPTC was synthesized from TMPTGE and CO₂ in the presence of tetrabutylammonium bromide as catalyst in ethyl acetate. The solution was then washed with a water and brine solution and dried with magnesium sulfate. The solvent was then evaporated. PHU-5CC was then synthesized from TMPTC, 4,9-dioxa-1,12-dodecanediamine with DBTDL as catalyst.

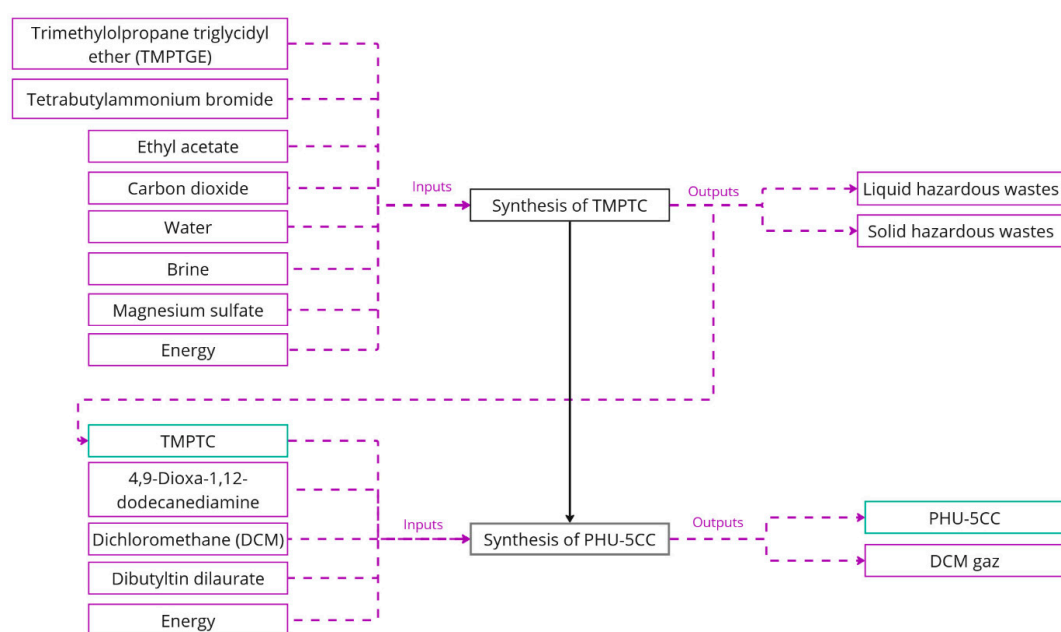


Figure 2. A flow diagram for PHU-5CC. A graphical representation of the material, energy and emission flows associated with the various stages in the life cycle of PHU-5CC.

The quantities and protocol for the TMPTC compound are taken from the study of Coste et al. [60], and the synthesis of PHU-5CC from the work of Bakkali-Hassani et al. [52]. The LCIs for the production of PHU-5CC are listed in Table 2. LCIs for the molecules tetrabutylammonium bromide, trimethylolpropane triglycidyl ether, DBTDL and 4,9-dioxa-1,12-dodecanediamine did not exist in our database and had to be created (Tables S1 and S2). For tetrabutylammonium bromide and 4,9-dioxa-1,12-dodecanediamine, datasets for similar compounds were available in Ecoinvent and were used as proxies (ethylene bromide and hexamethylenediamine, respectively). The protocol for the synthesis of TMPTGE can

be found in the patent from Roth et al. [66]. In this synthesis, the authors used tin difluoride, but more recently tin difluoride has been replaced by the catalyst benzyltriethylammonium chloride (TEBAC) [67]. The flow diagram for TEBAC can be found in the study of Chen et al. [68] (Table S1). The TMPTGE inventory was then completed using data from a similar synthesis in Ecoinvent (Table S1). The DBTDL inventory was found in the study of Glotz et al. [69] (Table S2). The electricity and heat for the synthesis of TMPTC were calculated on the basis of a similar synthesis in Ecoinvent, using Equations (1) to (3) (Table S3), while the electricity for PHU-5CC synthesis was measured directly using a wattmeter. Furthermore, for the synthesis of PHU-5CC, according to the study of Glotz et al. [69], 0.2% of raw material input goes to air emissions. Thus, we supposed that 0.2% of DCM went to air emissions.

Table 2. Life cycle inventories of the production of PHU-5CC.

Name	Process Unit/Emitted Substances	Input	Output	Unit
Production of TMPTC				
TMPTC	PHU—TMPTC	-	387.7	g
Trimethylolpropane triglycidyl ether	PHU—trimethylolpropane triglycidyl ether	300	-	g
Tetrabutylammonium bromide	Ethylene bromide {RER} market (Ecoinvent)	9.596	-	g
Ethyl acetate	Ethyl acetate {GLO} market (Ecoinvent)	108.2	-	g
Carbon dioxide	Carbon dioxide, liquid {RER} market (Ecoinvent)	131	-	g
Water	Water, deionized {Europe without Switzerland} market (Ecoinvent)	320	-	g
Brine solution	Sodium chloride, brine solution {GLO} market (Ecoinvent)	8	-	g
Magnesium sulfate	Magnesium sulfate {GLO} market (Ecoinvent)	20	-	g
Electricity	Electricity, medium voltage {RER} market (Ecoinvent)	0.07871962	-	kWh
Heat	Heat, district or industrial, natural gas {RoW} market (Ecoinvent)	0.0372	-	MJ
Liquid wastes	Spent solvent mixture {Europe without Switzerland} market (Ecoinvent)	-	436.2	g
Solid wastes	Hazardous waste, for incineration {Europe without Switzerland} market (Ecoinvent)	-	20	g
Production of PHU-5CC				
PHU-5CC	PHU-5CC	-	17	g
TMPTC	PHU—TMPTC	10	-	g
4,9-dioxa-1,12-dodecanediamine	Hexamethylenediamine {GLO} market (Ecoinvent)	5.71	-	g
Dichloromethane	Dichloromethane {RER} market (Ecoinvent)	5.32	-	g
Dibutyltin dilaurate	PHU—dibutyltin dilaurate	1.71	-	g
Electricity	Electricity, medium voltage {RER} market (Ecoinvent)	0.54	-	kWh
Liquid wastes	Spent solvent mixture {Europe without Switzerland} market (Ecoinvent)	-	5.31	g
Air emissions				
Methane, dichloro-, HCC-30		-	0.01064	g

3.2. PHU-6CC-Inventories

Figure 3 shows the various steps involved in the production of PHU-6CC. First, the MC6 monomer was synthesized using TMPAE, THF, ethyl chloroformate and triethylamine. The solution was then filtered to remove the salts formed, washed with ethyl acetate, a solution of hydrochloric acid, a saturated solution of sodium bicarbonate, brine and dried with magnesium sulfate. The TriC6 monomer was then synthesized from MC6, 1,4-dioxane, AIBN and TMPTM, washed with ethyl acetate and distilled water and dried with magnesium sulfate. PHU-6CC was then synthesized from the TriC6 monomer, *m*-XDA and a MeOK catalyst.

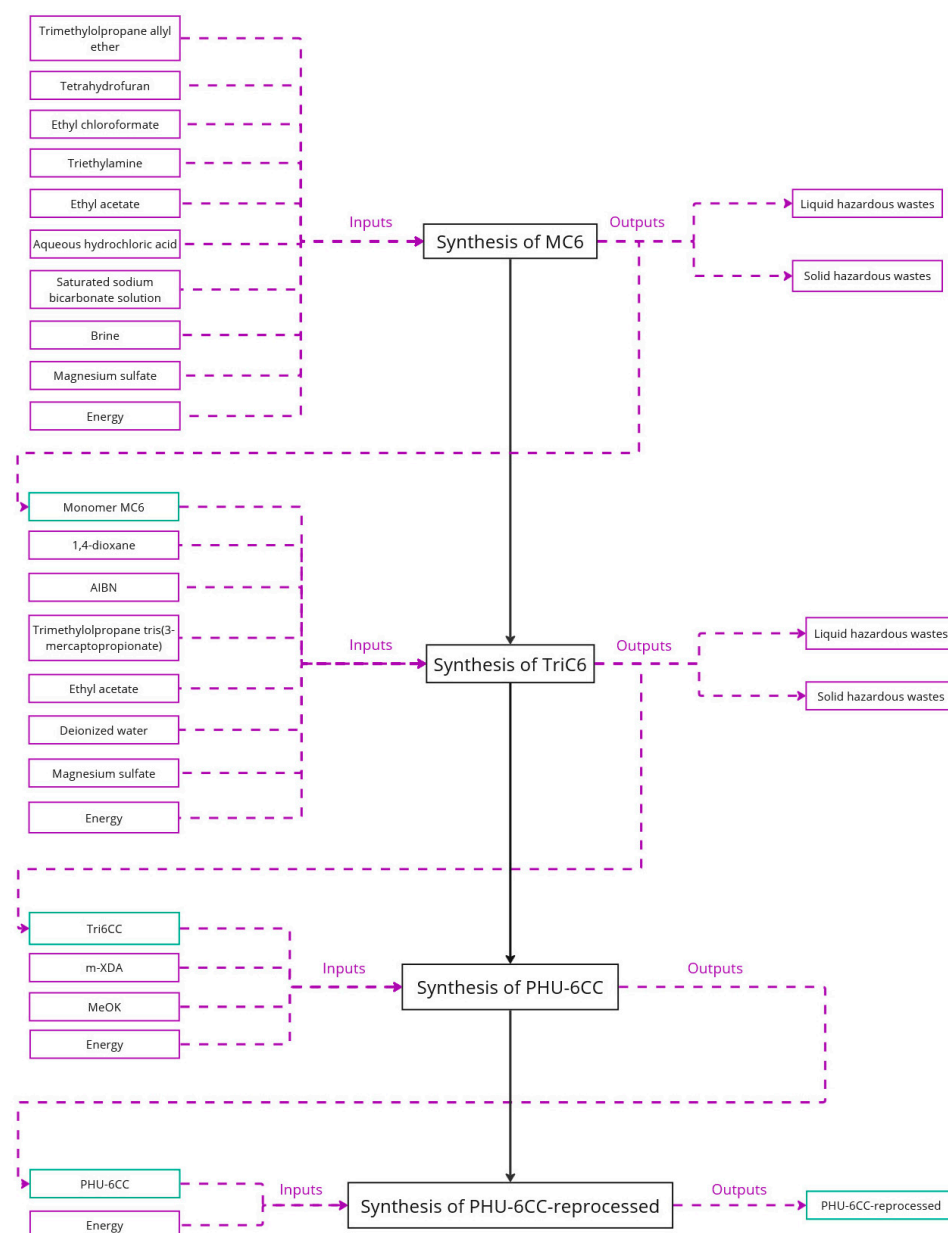


Figure 3. A flow diagram for PHU-6CC. A graphical representation of the material, energy and emission flows associated with the various stages in the life cycle of PHU-6CC.

The amounts of each compound were calculated on the basis of the synthesis described in the study of Coste et al. [61] and studies carried out in our laboratories for the synthesis of PHU-6CC. LCIs for the manufacture of PHU-6CC are presented in Table 3. Background datasets for trimethylolpropane allyl ether, ethyl chloroformate, AIBN, trimethylolpropane tris(3-mercaptopropionate), *m*-XDA and MeOK were not provided in Ecoinvent, and specific inventories had to be created (Tables S4–S8). For trimethylolpropane allyl ether, we made an approximation with a molecule already existing in the database which would have similar environmental impacts to our molecule. As for ethyl chloroformate, its synthesis was taken from a patent from Rozsa et al. [70] and electricity consumption and heat were calculated on the basis of a similar synthesis found in the database (Table S4). The AIBN inventory was taken from the work of Ang et al. [71] (Table S5). As there was no similar molecule in the database and no LCA in the scientific literature, a generic average dataset was used to represent trimethylolpropane tris(3-mercaptopropionate). The LCI for *m*-XDA was found in the study of Liang et al. [55], but the Raney nickel inventory was missing

and was found in the work of Lavery et al. [72] (Tables S6 and S7). Sodium methoxide was present in the database, so all its input/output quantities were recalculated using potassium instead of sodium to create the MeOK inventory. As for the calculation of the electricity consumption required for the MC6 and TriC6 syntheses, these were calculated using Equations 1 to 3 (Table S3). The electricity required for PHU-6CC synthesis was measured directly using a wattmeter.

Table 3. Life cycle inventories for production of PHU-6CC.

Name	Process Unit/Emitted Substances	Input	Output	Unit
<i>Production of MC6</i>				
PHU-MC6	PHU-MC6	-	45.6	g
Trimethylolpropane allyl ether	Dimethyl hexanediol {GLO} market (Ecoinvent)	43.6	-	g
Tetrahydrofuran	Tetrahydrofuran {GLO} market (Ecoinvent)	248.6	-	g
Ethyl chloroformate	PHU—ethyl chloroformate	78.7	-	g
Triethylamine	Triethylamine {GLO} market (Ecoinvent)	75.9	-	g
Ethyl acetate	Ethyl acetate {GLO} market (Ecoinvent)	144.3	-	g
Hydrochloric acid solution (0,5M)	Hydrochloric acid, without water, in 30% solution state {RER} market (Ecoinvent)	8.6	-	g
Sodium bicarbonate solution	Sodium bicarbonate {RER} market (Ecoinvent)	11.2	-	g
Brine solution	Sodium chloride, brine solution {GLO} market (Ecoinvent)	8.0	-	g
Water	Water, deionized {Europe without Switzerland} market (Ecoinvent)	472.8	-	g
Magnesium sulfate	Magnesium sulfate {GLO} market (Ecoinvent)	20	-	g
Electricity	Electricity, medium voltage {RER} market (Ecoinvent)	0.052192745	-	kWh
Liquid wastes	Spent solvent mixture {Europe without Switzerland} market (Ecoinvent)	-	893.5	g
Solid wastes	Hazardous waste, for incineration {Europe without Switzerland} market (Ecoinvent)	-	51.24	g
<i>Production of TriC6</i>				
TriC6	PHU-TriC6	-	56	g
MC6	PHU-MC6	40.05	-	g
1,4-dioxane	Dioxane {RER} market (Ecoinvent)	66.1	-	g
Azobisisobutyronitrile	PHU—azobisisobutyronitrile	1.64	-	g
Trimethylolpropane tris(3-mercaptopropionate)	Chemical, organic {GLO} chemical production, organic (Ecoinvent)	24.43	-	g
Ethyl acetate	Ethyl acetate {GLO} market (Ecoinvent)	144.3	-	g
Water	Water, deionized {Europe without Switzerland} market (Ecoinvent)	160	-	g
Magnesium sulfate	Magnesium sulfate {GLO} market (Ecoinvent)	20	-	g
Electricity	Electricity, medium voltage {RER} market (Ecoinvent)	0.037221292	-	kWh
Liquid wastes	Spent solvent mixture {Europe without Switzerland} market (Ecoinvent)	-	370.5	g
Solid wastes	Hazardous waste, for incineration {Europe without Switzerland} market (Ecoinvent)	-	20	g
<i>Production of PHU-6CC</i>				
PHU-6CC	PHU-6CC	-	8.4	g
TriC6	PHU-TriC6	7	-	g
m-xylylenediamine	PHU-m-xylylenediamine	1.4	-	g
Potassium methoxyde	PHU—potassium methoxyde	0.0637	-	g
Electricity	Electricity, medium voltage {RER} market (Ecoinvent)	0.27	-	kWh

4. Impact Assessment

4.1. PHU-5CC Synthesis

In the production of PHU-5CC (Figure 4), electricity, DBTDL and TMPTC can be identified as the main contributors to most environmental indicators. The various environmental impacts from electricity are generated from its production to its consumption. Electricity generation, which comes from a variety of sources (coal, natural gas, nuclear, hydroelectric, wind, solar, etc.), has different environmental impacts depending on whether it comes from renewable resources or not [73,74]. The extraction of fossil fuels [75] or uranium [76] poses environmental problems, notably through the use of fossil resources, water consumption and greenhouse gas (GHG) emissions. Once electricity has been produced, which also implies GHG emissions [77], the infrastructures needed to transport it also contribute to the various impacts, through their construction (in addition, loss of biodiversity through space occupation) and maintenance [78,79]. The DBTDL and diamine also contribute to the impacts of PHU-5CC synthesis.

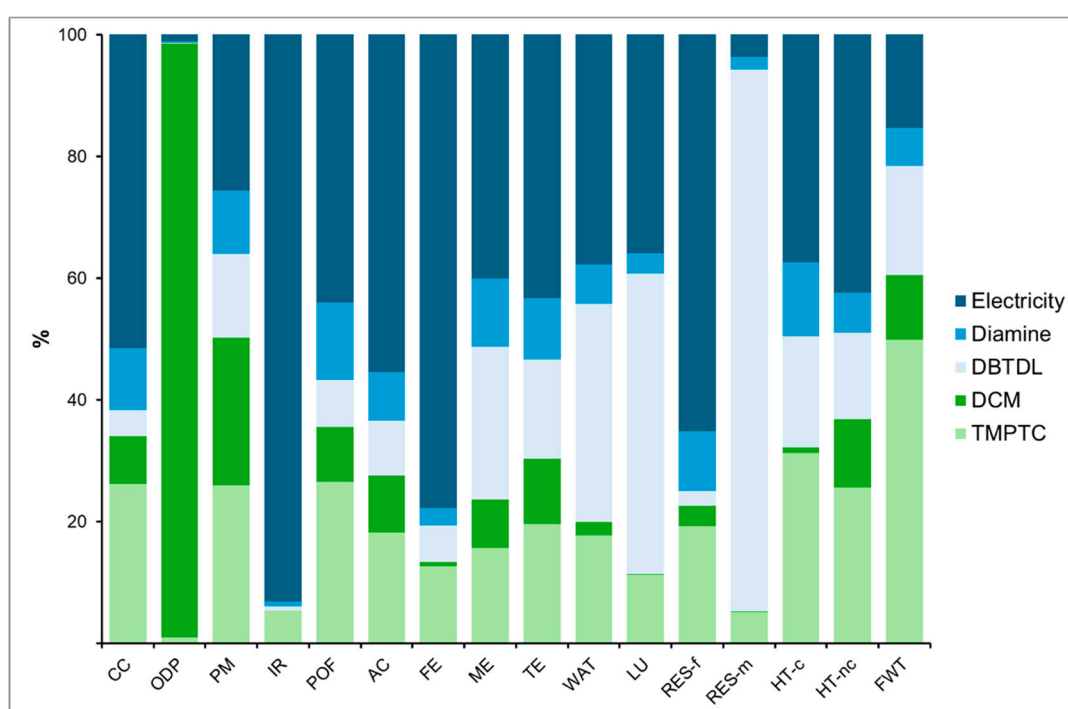


Figure 4. Impact assessment for synthesis of PHU-5CC—contribution analysis. Acronyms summarized in Table 1.

The DBTDL used in the synthesis is a catalyst based on tin, a heavy metal whose extraction is very harmful to the environment and human health. The process generates significant GHG emissions and requires large amounts of energy, often from non-renewable sources [80]. The synthesis of DBTDL is also energy-consuming due to the conditions it requires, such as high temperatures and the use of organic solvents, as well as the treatment of the toxic by-products generated [81]. DBTDL is also harmful to human health as it is neurotoxic and acts as an endocrine disruptor [82]. Though DBTDL accounts for roughly only 7 wt% of the material inputs for the PHU synthesis, its contribution to the calculated impacts is significantly higher for almost all the indicators. This means that the use of this compound is clearly a hotspot, and that efforts to reduce or substitute DBTDL could result in significant footprint improvement. However, though tests were made with other types of catalysts (e.g., bases and acid organocatalysts) that could have a lighter impact and/or could be used in lower amounts, DBTDL, an organometallic Lewis acid, proved to be the

only efficient catalyst for promoting the desired exchange reaction due to its activation of both alcohol and carbamate moieties through a coordinated transition state.

Dichloromethane is also a major contributor to ozone depletion, as it is a volatile organic compound (VOC) that releases chlorinated substances into the atmosphere. Ozone depletion refers to the depletion of the stratospheric ozone layer due mainly to anthropogenic emissions such as chlorofluorocarbons (CFCs) and halons. Stratospheric ozone absorbs most of the sun's harmful ultraviolet rays. A reduction in this layer, which protects us from these rays, would increase the risk of cancer and skin problems for humans, and have an impact on various ecosystems [83].

4,9-dioxa-1,12-dodecanediamine, the diamine used, is a corrosive diamine that can have significant effects on the environment, health and particularly on ecosystems if it is found in soils and water, where it can alter pH [84]. In addition, its synthesis contributes to global warming through the release of greenhouse gases.

Since TMPTC is the main component of PHU formulation, and a major contributor to its impacts, a contribution analysis on TMPTC production may be useful. In TMPTC synthesis (Figure 5), TMPTGE production is obviously the main contributor to all the indicators. TMPTGE's impacts are mainly due to the reagents used in its synthesis, particularly epichlorohydrin. The production of epichlorohydrin impacts global warming as the processes involved are energy-consuming and contribute significantly to greenhouse gas (GHG) emissions [85]. In addition, its production and use lead to the release of chlorinated compounds that acidify the environment, with consequences for ozone depletion [86]. As far as health is concerned, epichlorohydrin is a toxic substance which can cause skin irritation and respiratory disorders in the event of direct contact [85,86].

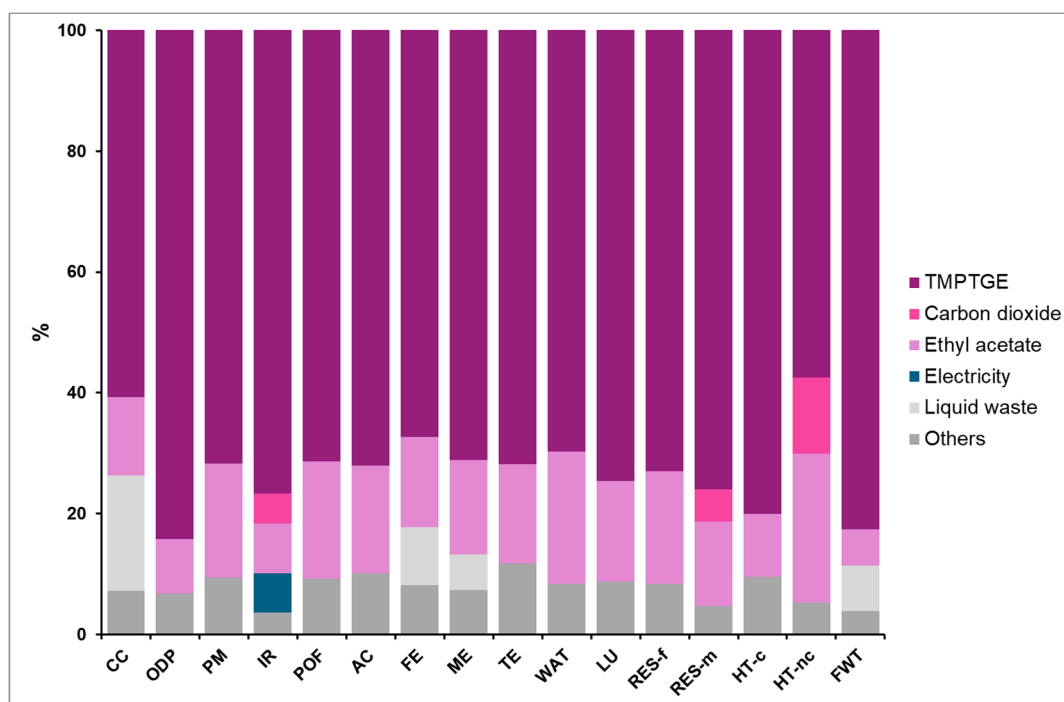


Figure 5. Impact assessment of TMPTC synthesis—contribution analysis. Acronyms summarized in Table 1.

The ethyl acetate, the solvent used in carbonate synthesis, and DCM used in the synthesis of PHU-5CC also contribute to impacts in several categories. Volatile organic compounds (VOCs) such as these solvents evaporate easily into the atmosphere, affecting human health and polluting the air. Their production is energy-consuming and relies on petro-based raw materials, which increases GHG emissions. Moreover, if the solvents are

not properly treated and eliminated, they can contaminate soil and water, with negative consequences for biodiversity and ecosystems. As these solvents are considered hazardous waste due to their toxicity and flammability, their treatment requires special attention to avoid environmental contamination. In addition, some solvents release toxic by-products during degradation or combustion, adding to air pollution [87,88]. The most promising ways to reduce the impacts of TMPTC (and hence of PHU-5CC) would therefore be to investigate the possibility of using less ethyl acetate or an alternative, more friendly solvent, and of using a TMPTGE or an alternative molecule with similar functionality that would not require epichlorohydrin for its production.

4.2. PHU-6CC Synthesis

In the production of PHU-6CC (Figure 6), the synthesis of the carbonate TriC6 is the main contributor. Electricity contributes significantly, for the reasons already cited, to the synthesis of PHU-5CC. The impact of diamine on the final PHU product (Figure 6) is relatively low, especially when compared with carbonate production, which is a multi-step and solvent-intensive synthesis. Lastly, the catalyst used has almost no impact on human health or the environment in the case of the synthesis of PHU-6CC.

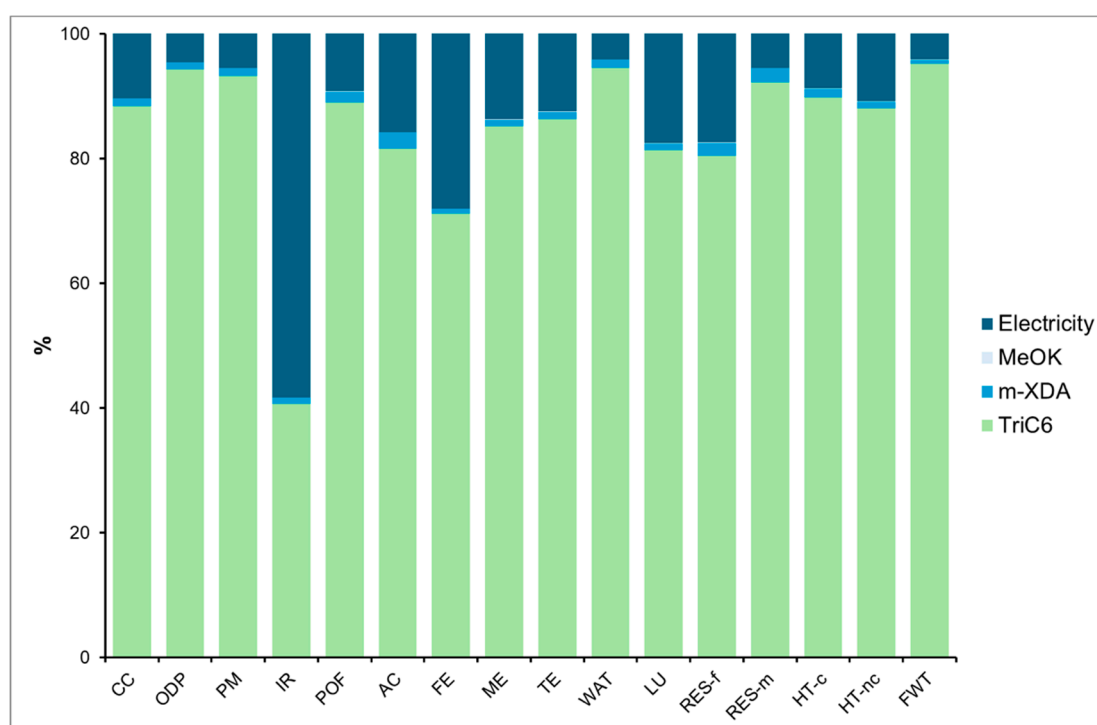


Figure 6. Impact assessment of synthesis B—contribution analysis. Acronyms summarized in Table 1.

While the contribution of the catalyst DBTDL to the impacts of PHU-5CC was significant, MeOK is here used in much smaller quantities, and its contribution to the impacts of the PHU is marginal.

Regarding the synthesis of TriC6 (Figure 7), the use of ethyl chloroformate, a phosgene derivative, has been widely criticized due to its toxicity [89]. Ethyl chloroformate is a highly reactive and corrosive reagent, requiring strict precautions for its use. However, although its use is indeed a cause for concern, it actually appears that the solvents used in the synthesis contribute more to the calculated environmental impact. The mass contribution of ethyl chloroformate in TriC6 synthesis is only 5%, compared with 44% for the solvents, which is why solvents have a greater impact. On the other hand, taking the climate change impact category as an example, the solvents account for 80% of the total impact while

ethyl chloroformate accounts for just 5%. If we reduce the proportion of solvents to that of ethyl chloroformate, they still have a greater impact than ethyl chloroformate. These solvents contribute to the different impact categories for the same reasons as the use of ethyl acetate in the synthesis of TMPTC mentioned above. This raises the industrial concern of whether these solvents can be fully recycled in order to reduce their environmental impact. In addition, AIBN has the most significant impact in the ozone depletion category. Its contribution to this impact category comes from its synthesis, which requires the use of dichloromethane and bromine.

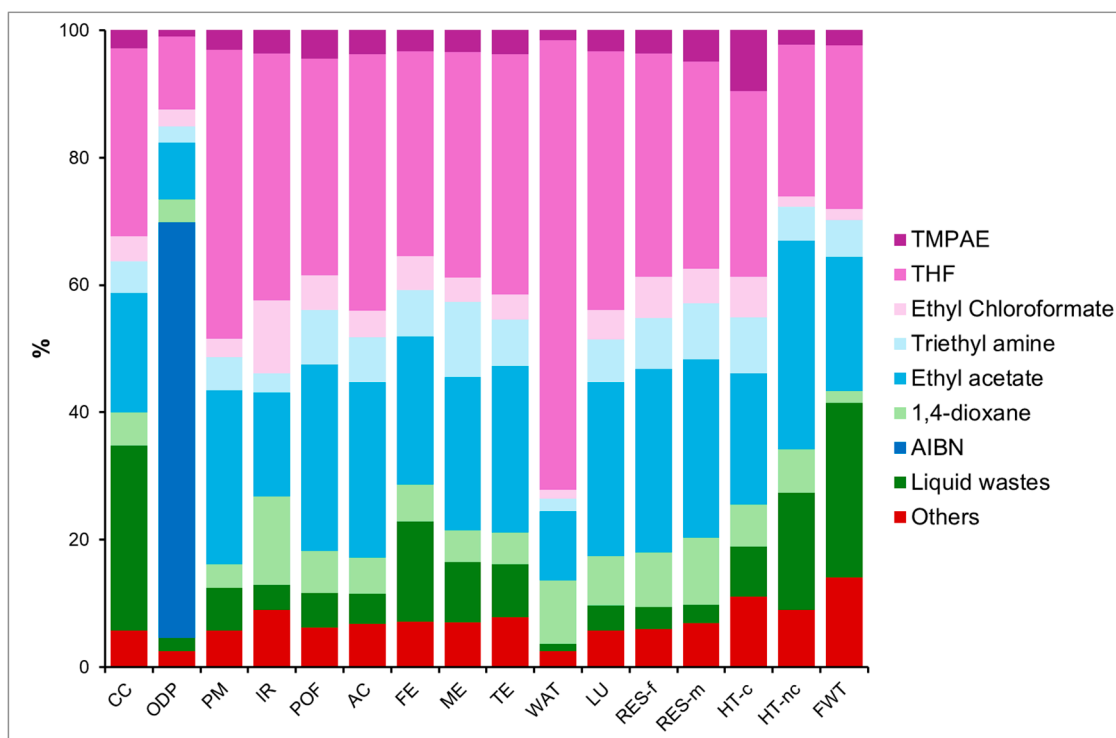


Figure 7. Impact assessment of TriC6 synthesis—contribution analysis. Acronyms summarized in Table 1.

4.3. Comparison of PHU-5CC Vs. PHU-6CC Synthesis

4.3.1. Global Vision of Impacts of Both Syntheses

The calculated impacts are presented for syntheses carried out under the same conditions (80 °C for 24 h) defined for this study (Figure 8). Except for the ozone depletion (ODP) and resource use, minerals and metals (RES-m) impact categories, PHU-6CC synthesis has a greater impact. To identify the impact categories that are the most significant for the studied system, normalized results are shown in Figure 9. Normalization is a procedure used in LCA to evaluate the relative importance of the results obtained for all the indicators of the considered system. It consists of normalizing the results obtained based on the impacts of an average world citizen (global emissions and extracted resources required for one person in the world per year [59,90,91]). In the present case, Figure 9 reveals that the ODP and LU indicators are much less significant for the studied system than, e.g., FE, and that the differences observed in these two indicators between the two systems are not worth a thorough investigation. On the other hand, the CC, FE, RES-f, HT-c and FWT categories appear to have the most significant impacts.

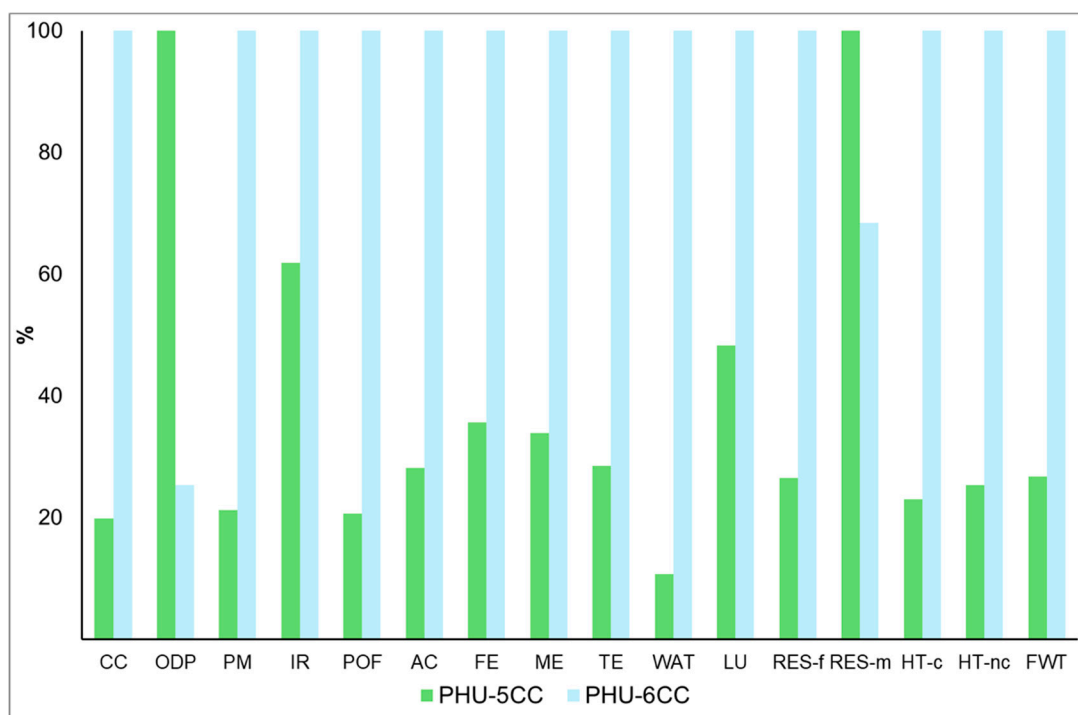


Figure 8. Impact assessment—compared cradle-to-gate impacts of PHU-5CC and PHU-6CC. Acronyms summarized in Table 1.

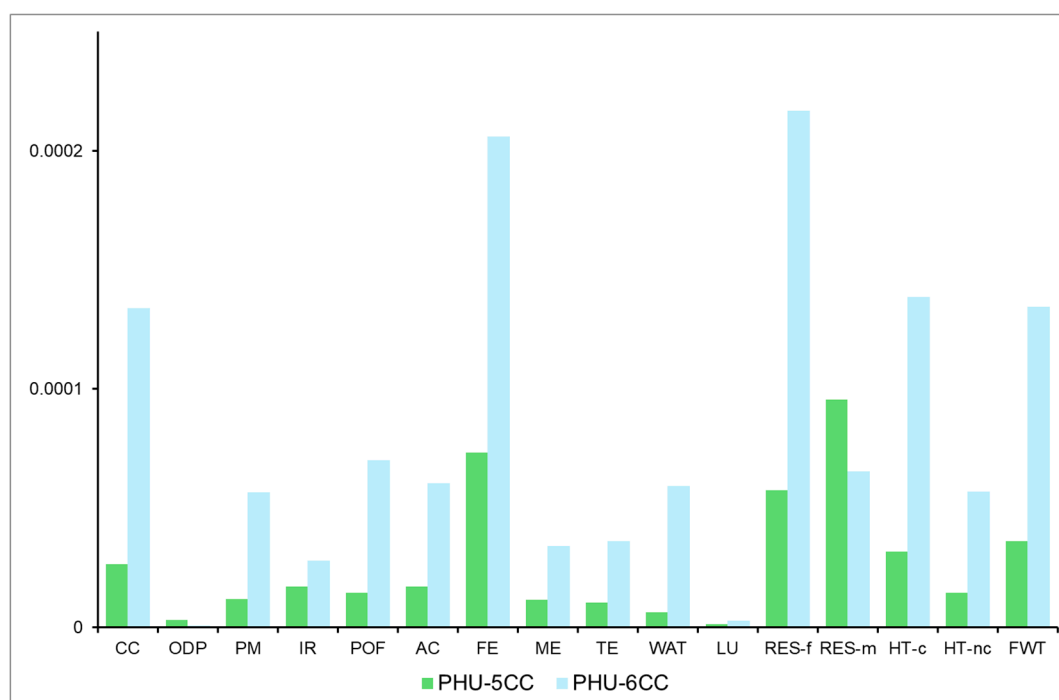


Figure 9. Compared cradle-to-gate impacts of PHU-5CC and PHU-6CC—normalized results. Acronyms summarized in Table 1.

In order to better understand where the differences between the impacts arise from, a more detailed comparative contribution analysis is proposed below, focusing on the CC, PM, FE, RES-f and RES-m indicators. This selection is based on the respective classification of the indicators (cf. Table 1), the calculated differences between the two syntheses for all the

indicators (cf. Figure 8) and the results of the normalization (Figure 9). The model inputs contributing to the impacts are grouped into different categories, as explained in Table S8.

Climate Change

The “climate change” impact category concerns the effect of greenhouse gas (GHG) emissions into the atmosphere, leading to global warming. This impact category measures the influence of human activities, expressed in kg of CO₂ equivalent on the atmosphere’s radiative forcing, i.e., the capacity of emitted gases to absorb the infra-red radiation emitted by the Earth as a result of the absorption of solar radiation. The increase in radiative forcing is responsible for global warming, with consequences for ecosystems, health and material goods [83,92].

Figure 10 shows the impact of both PHU-CANs. The categories shown in the legend include all the reagents, electricity, solvents, etc., required for carbonate synthesis, up to the production of PHU. The impact of the reagents is similar for both syntheses. The impact on the climate is higher for PHU-6CC, mostly due to the large use of solvents (THF, ethyl acetate), their volatility and toxicity, as mentioned above, and their treatment as waste. In the case of PHU-6CC synthesis, the quantity of solvent used is much higher than for PHU-5CC synthesis (Tables 2 and 3), which explains the higher impact.

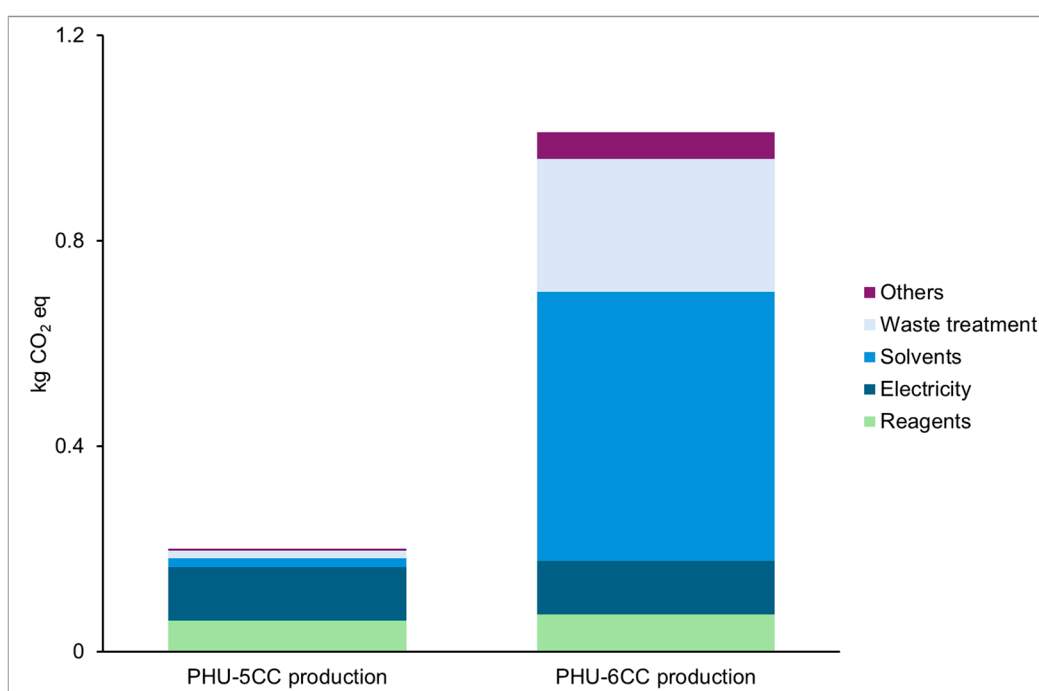


Figure 10. Compared climate change impacts for production of PHU-5CC and PHU-6CC.

Particulate Matter

The particulate matter category refers to fine particles suspended in the air. These particles are classified according to their size. For instance, PM_{2.5} refers to particles with a diameter of less than 2.5 µm. These particles come from various sources and steps in the synthesis of PHU-CANs. Inhalation of these particles by humans is toxic and causes various health problems, such as respiratory and cardiovascular diseases. This indicator relates to the human health effects associated with the exposure of humans to PM_{2.5} during the life cycle of the studied system, and results are expressed as disease incidence [92].

Figure 11 shows the comparison of the two PHU-CANs for the particulate matter impact category. The categories shown in the legend include all the reagents, electricity,

solvents, etc., required for carbonate synthesis, up to the production of PHU. PHU-6CC synthesis has the highest impact in this category due to the higher number of compounds, especially solvents, required to synthesize 6CC, which emit particles smaller than $2.5\ \mu\text{m}$ and generate sulfur dioxide. Solvents influence the particulate matter category in particular via the emission of volatile compounds into the air, which contribute to the formation of fine particles in the air either by reacting with atmospheric molecules or during their production and elimination. Moreover, in this category, the impacts generated by electricity are caused by its production from fossil fuels such as coal, which leads to the emission of fine particles and to the building of infrastructure [93].

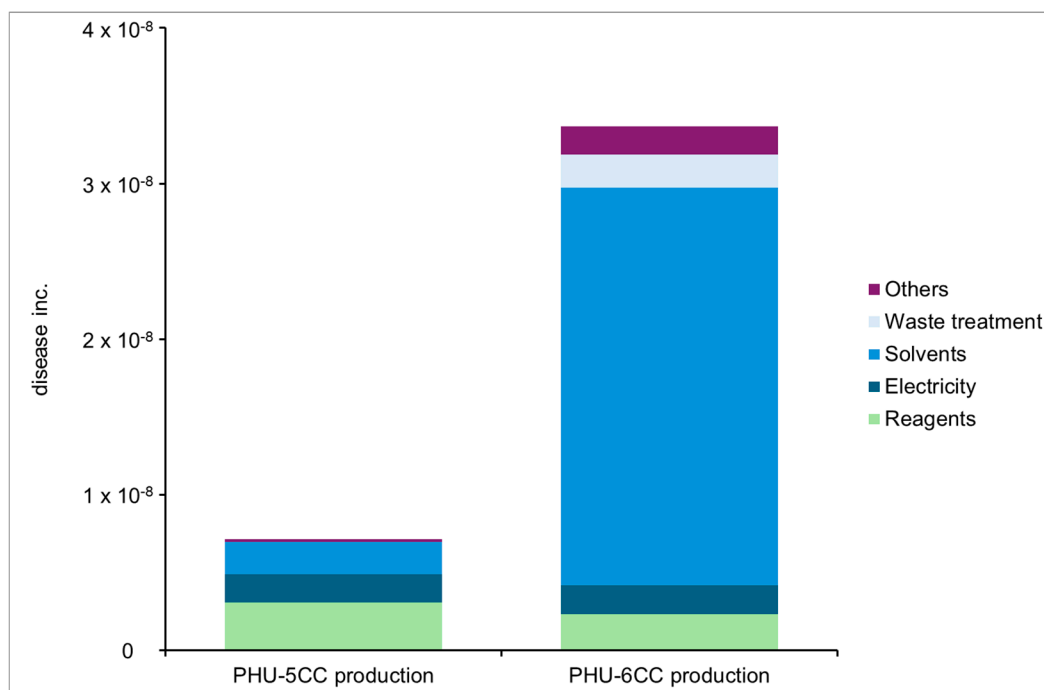


Figure 11. Compared particulate matter impacts for production of PHU-5CC and PHU-6CC.

Eutrophication, Freshwater

The freshwater eutrophication category is an indicator of the enrichment of freshwater ecosystems with nutrients derived from the emission of compounds containing nitrogen or phosphorus (P), and is expressed in kg P eq. Nutrient overload can cause disequilibrium in ecosystems, favoring the proliferation of algae and other aquatic plants, which is not without consequences [94].

PHU-6CC has the highest impact on this indicator (Figure 12). During solvent production, emissions of polluting substances into the air, soil and water can occur [95,96]. These solvents can also contaminate water if they are not properly treated. Moreover, chemicals containing nitrogen or phosphorus compounds may be discharged into water-courses, contributing to eutrophication. The electricity-related impacts are mainly due to the extraction of fossil fuels and their combustion, which emits nitrogen and phosphate compounds [97,98].

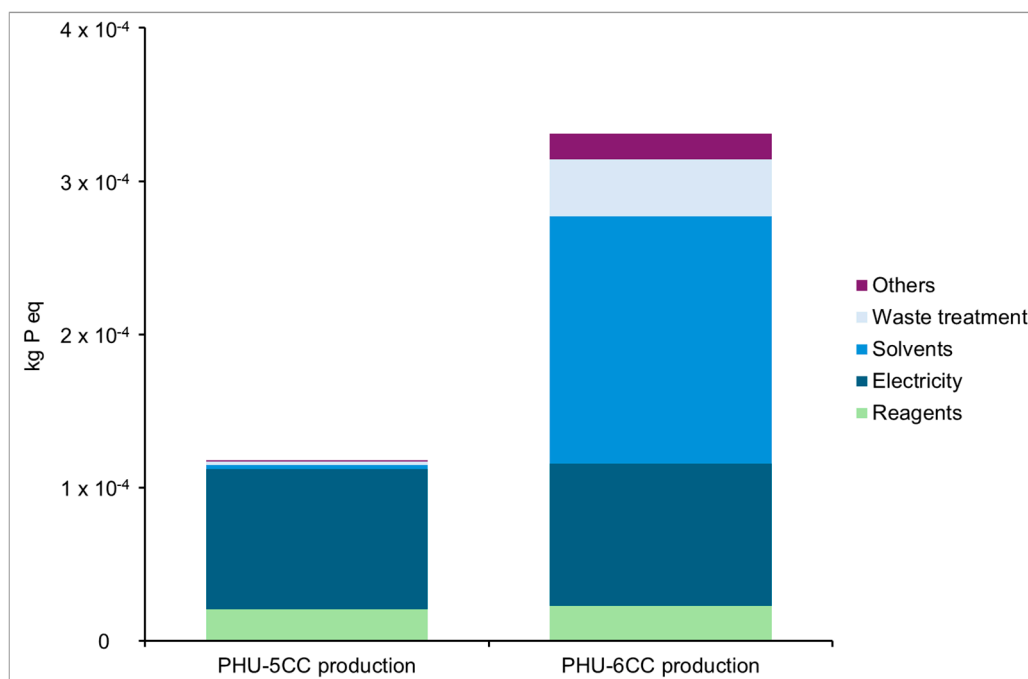


Figure 12. Compared eutrophication freshwater impacts for production of PHU-5CC and PHU-6CC.

Resource Use, Fossil

The resource use, fossil (RES-f) category is an indicator of natural fossil fuel resource depletion (abiotic) and is expressed in MJ. This category is highlighted by the normalization in Figure 9. The higher impacts for the synthesis of PHU-6CC in this category are due to its use of solvents and the need for several steps in the carbonate synthesis (Figure 13). Thus, the production of PHU-6CC requires much more non-renewable materials than that of PHU-5CC. Moreover, electricity needs a high quantity of fossil fuels for its production in terms of combustible fuels or infrastructures.

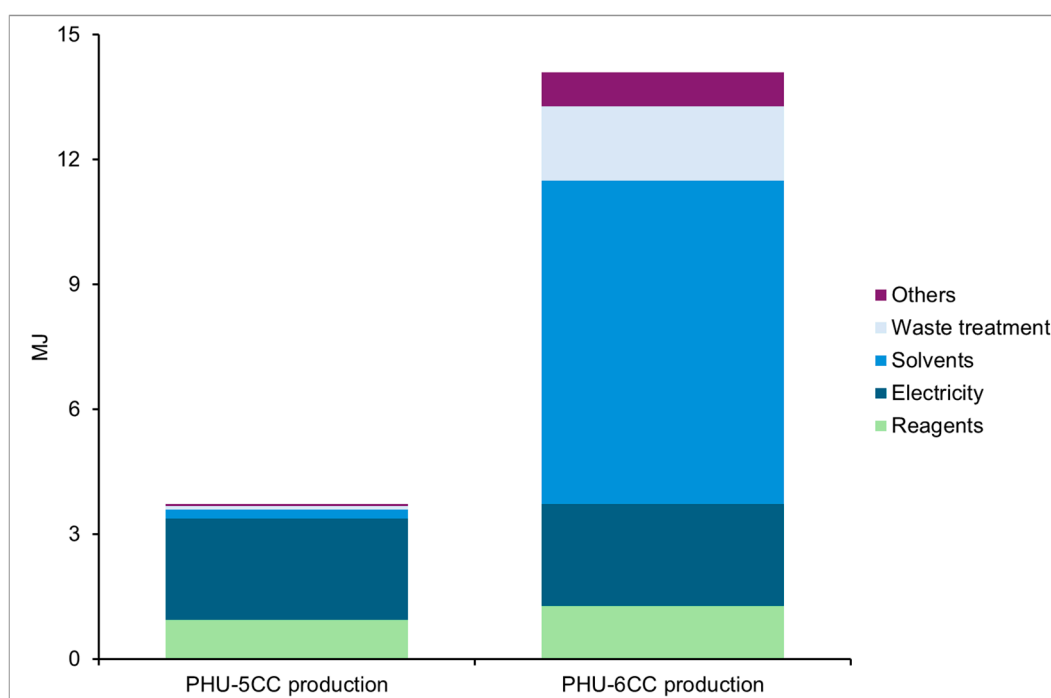


Figure 13. Compared resource use, fossil impacts for production of PHU-5CC and PHU-6CC.

Resource Use, Minerals and Metals

The resource use, minerals and metals (RES-m) category is an indicator of non-renewable resource depletion (abiotic), especially metals and minerals extracted from the soil [99,100]. The environmental impact of this category is calculated from the extraction of these materials to their use and end of life. The results are expressed in kilograms of antimony equivalents (kg Sb eq.)

This category is presented in Figure 14 since it is the indicator with the highest normalized score for PHU-5CC, as seen in Figure 9. This impact is predominantly caused by the use of DBTDL, which requires the extraction of tin and its transformation into organometallic compounds through complex chemical processes. The solvents used more massively in the synthesis of PHU-6CC are the main contributors to this indicator for this system.

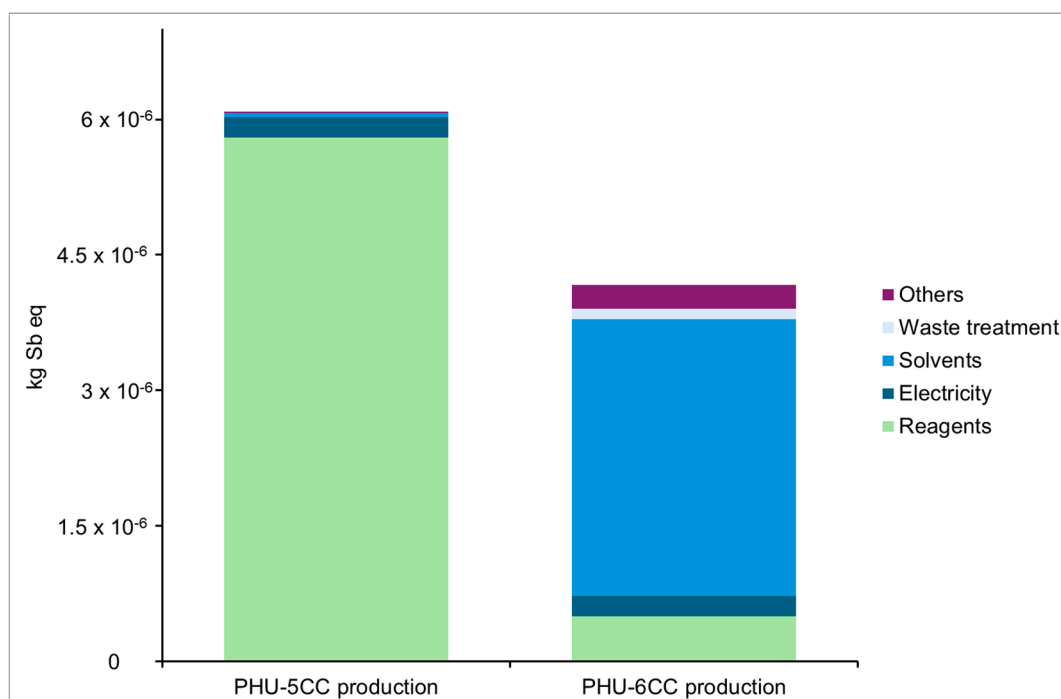


Figure 14. Compared resource use, minerals and metals impacts for PHU-5CC and PHU-6CC syntheses.

Preliminary Conclusions

Under laboratory conditions, and with identical curing parameters for both syntheses, the environmental footprint of PHU-5CC synthesis was the lowest. In both syntheses, the synthesis of carbonates and electricity consumption were the primary contributors to environmental impacts. The synthesis of the six-membered cyclic carbonate had a greater impact due to the necessity of two synthesis steps and the large quantities of solvents used. Notably, the use of phosgene in the synthesis had a lesser impact than the solvents employed. In both carbonate (bio- or petro-based) and PHU-CAN syntheses, solvents emerged as the main contributors to harmful environmental impacts because of their volatility and toxicity.

This study also underscores the significance of catalyst selection. The PHU-6CC synthesis utilized a more environmentally friendly catalyst, resulting in lower impacts, while the PHU-5CC synthesis employed a metal catalyst that contributes to the depletion of non-renewable resources and environmental pollution.

All these findings highlight the primary sources of environmental impacts, particularly those associated with electricity use and solvents. However, these laboratory-scale

syntheses are not optimized, and some parameters that seem significant may carry less weight when scaled up for industrial processes. To validate the robustness of the results obtained at the lab scale, sensitivity studies were conducted, as detailed below.

5. Sensitivity Studies

5.1. Variation in Synthesis Time

The LCA study described above concerns two PHU-CANs cured for 24 h to ensure high carbonate conversion. In reality, the curing time of PHUs differs according to the carbonate used. Tomita et al. [30] studied the reactivity of 5CC and 6CC carbonates and showed that the curing times for carbonate conversions of over 90% could be reduced by at least a factor of two by using 6CC instead of 5CC in PHU synthesis. In our case, despite the increase in reaction rate by the catalysts in the first 20 min, the production of PHU-5CC remains slow to achieve a conversion of over 90%. On the other hand, for the PHU-6CC synthesis, we carried out model reactions and infra-red monitoring to get an idea of the time actually needed for the synthesis. The results of the model reaction between TriC6 and a simple amine showed that the carbonate was consumed in 15 min; however, in a network, the reaction rate is slower due to increased steric hindrance. Even if infra-red monitoring is not an exact technique, we can consider that the reaction could be complete between 4 and 8 h for PHU-6CC, but would still require a reaction time close to 24 h for PHU-5CC. Thus, considering the reactivity of carbonates, the impacts were calculated for 4 and 8 h for the impact categories described above and are represented in Figure 15.

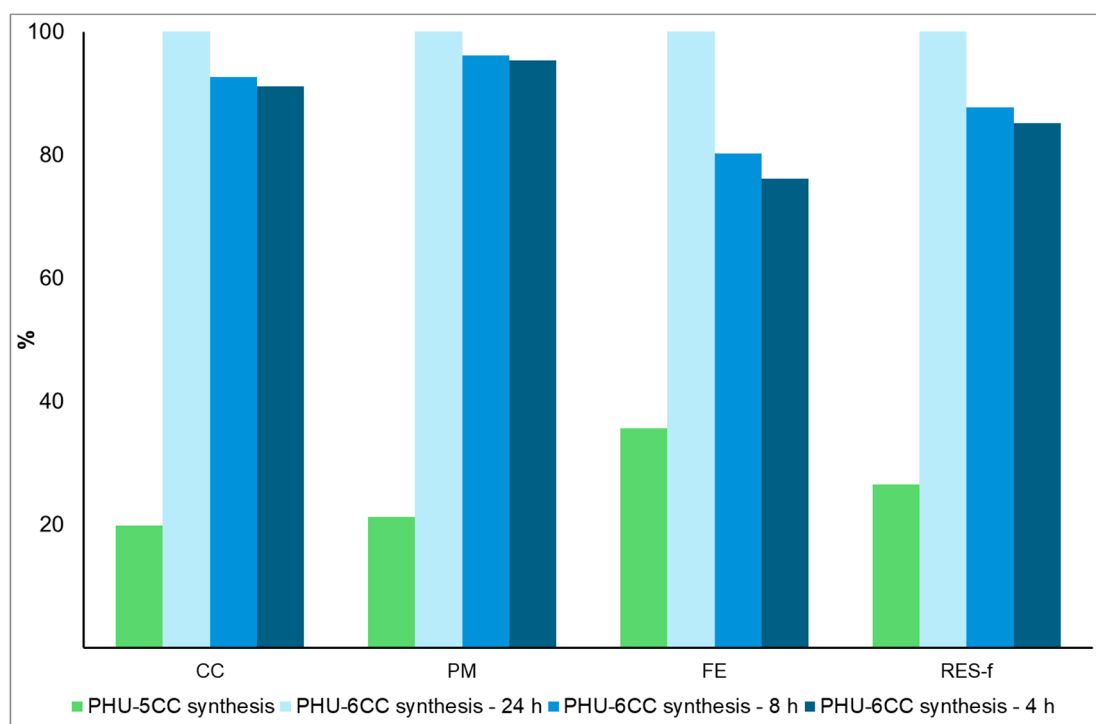


Figure 15. Impact assessment—sensitivity analysis of PHU-5CC synthesis with different reaction times of PHU-6CC synthesis.

By shortening the reaction time, the impacts of PHU-6CC synthesis were somewhat reduced, but they remained higher than the impacts of PHU-5CC. On the other hand, there is only a slight difference between the 4 h and 8 h reaction times. The environmental footprints of PHU-6CC cured for 4 h or 8 h can be considered similar. Taking a look at the other categories (Figure S1), despite the optimized reaction time, PHU-6CC is also the most impactful. Although the higher reactivity of the carbonate shortens the reaction times, this

is not enough to compensate for the environmental impacts associated with its synthesis. As a result, the production of PHU-6CC always has a higher impact than that of PHU-5CC.

5.2. Industrial-Scale Optimization

In our context, electricity was not optimized for the size of the machine in relation to the 10 g of product. To take account of a more optimized electricity use process, we used some data from the scientific literature [101]. In this study, for 234 kg of product, only 11.03 kWh were consumed when using the hot press at 160 °C for 1h30. The PHU-CANs are directly cured in the hot press to produce homogeneous shape at 80 °C for 24 h. By reducing the amount of electricity in line with our product mass (10 g) and synthesis conditions (24 h), the order of magnitude of the energy actually used in industry could be estimated. This calculated value (0.0063 kWh) is still overestimated, given the difference in temperatures between the curing procedures. However, the order of magnitude is similar to that used for PHU synthesis in the project already carried out by Materia Nova's LCA team [56].

We have already seen that by reducing synthesis time, and therefore electricity, the impact of PHU-CANs is reduced, as seen in Figure 16. The second part of that graph is shown in Figure S2 for more clarity. This comparison shows that the reduction in energy consumption favors a more sustainable synthesis for PHU-CANs. Moreover, Figures S3 and S4 show that the contribution of electricity optimized in an industrial context in both syntheses has very little impact and could be neglected compared to the reagents. In this case, all the reagents used, the TMPTC, the diamine (4,9-dioxa-1,12-dodecanediamine), the catalyst DBTDL and the solvent dichloromethane (DCM), have significant impacts in each category for the PHU-5CC synthesis, while the carbonate synthesis has the greatest impact in the case of the PHU-6CC synthesis.

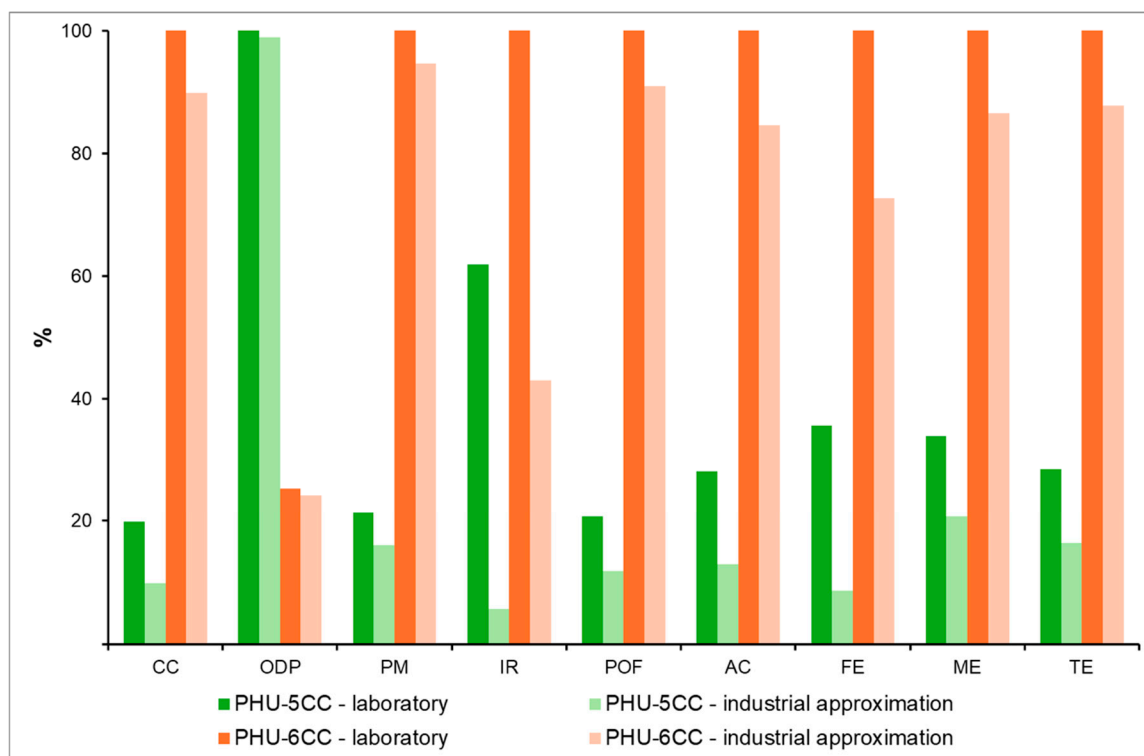


Figure 16. Life cycle impact assessment of 10 g PHU-CAN; comparison between laboratory and industrial approximation data.

In this study, solvents were identified as very significant contributors to the environmental impact of the syntheses. In our studies, the quantity of solvents was not modified in order to reduce the amount required without affecting the reaction. It would be interesting to study this issue in future work in order to optimize the syntheses. In an industrial context, the quantity could be reduced, or even recycled. The environmental footprint of materials would then be reduced. Increasingly, studies are focusing on solvent-free carbonate and PHU syntheses [102,103], which could also be a potential approach to reducing the environmental impacts of these materials.

5.3. *E-Factor Calculation for Both Syntheses, and Comparison with LCA*

The comparison of the *E-factors* for both syntheses allows us to determine which process generates less waste and thus presents a more environmentally favorable approach, from this point of view, to PHU synthesis, complementing the LCA study. The *E-factors* were calculated according to Equation (4), with values of 1.06 and 19.74 for the PHUs synthesized from 5CC and 6CC, respectively (Tables S9 and S10). The contribution of solvents to the *E-factor* was also determined using Equation (5). In the case of PHU-5CC, approximately 46% of the *E-factor* value is attributed to solvents, whereas this contribution rises to 92% for PHU-6CC (Tables S9 and S10). Overall, the synthesis using 6CC appears less environmentally friendly, primarily due to the significant use of solvents, which accounts for 92% of the *E-factor*. These results are consistent with the findings of the LCA study presented earlier.

6. Conclusions

In conclusion, when preparing 10 g of PHU-CAN at 80 °C over a 24 h period on a laboratory scale, the use of our 5CC synthesis offers a more environmentally sustainable approach than our 6CC synthesis. Although the PHU-CAN synthesized using 6CC has a shorter reaction time, this advantage does not offset the high environmental impact of the solvent used in the 6CC synthesis. Finally, the petro-based origin of the 6CC does not seem to have the most significant impact compared with the solvents. Beyond the origin of the compounds used (petro- and bio-based), our results highlight the significant impact of certain parameters, such as solvent usage, metal-based catalysts and reaction time, which lead to increased electricity consumption. Future research should explore alternative methods in order to reduce the environmental footprint of our lab-synthesized materials. This may involve the meticulous selection and reduction of solvents or their recycling, the use of more sustainable catalysts if necessary and the optimization of curing conditions to reduce energy consumption. The recovery of monomers by depolymerization could also be another alternative.

However, these results cannot be considered as a certain conclusion, since (i) a sensitivity study showed clearly that the possible optimization of the electricity and solvents would be the key for impact reduction in the footprint of the products and could lead to a more significant reduction for PHU-6CC than for PHU-5CC, and (ii) it should be noted that this study is incomplete in terms of life cycle thinking, as it is limited to the cradle-to-gate stage without including the application and end-of-life stages. Furthermore, it compares two systems on the assumption that they are isofunctional at equal mass, which is not absolutely certain until they have been tested in a specific application.

Research is ongoing and requires further development to optimize the syntheses and properties of the materials before they can be implemented in industrial applications. Despite the ongoing nature of the study, it is already providing valuable insights into optimizing environmental footprints by identifying hotspots and points of concern, such as solvent consumption or the necessity for the meticulous monitoring of reaction time.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/macromol5010012/s1>, Figure S1. Life Cycle Impact assessment of 10 g PHU-CAN – others impact categories. Figure S2. Life Cycle Impact assessment of 10 g PHU-CAN – Comparison between laboratory datas and industrial approximation datas. Figure S3. Impact assessment of PHU-5CC synthesis - contribution analysis - optimized electricity. Figure S4. Impact assessment of PHU-6CC synthesis - contribution analysis - optimized electricity. Table S1. Life cycle inventories of benzyltriethylammonium chloride and trimethylolpropane triglycidyl ether. Table S2. Life cycle inventories of dibutyltin dilaurate. Table S3. Energies calculations. Table S4. Life cycle inventory of ethyl chloroformate. Table S5. Life cycle inventory of AIBN. Table S6. Life cycle inventory of Raney Nickel. Table S7. Life cycle inventory of m-XDA. Table S8. Contributor’s inventory presented for each categories. Table S9. E-factor and solvent contribution to E-factor calculations for PHU-5CC. Table S10. E-factor and solvent contribution to E-factor calculations for PHU-6CC.

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Abbreviations

AC	Acidification
AIBN	Azobisisobutyronitrile
CAN	Covalent adaptable network
CC	Climate change
CFC	Chlorofluorocarbon
CO ₂	Carbon dioxide
DBTDL	Dibutyltin dilaurate
DCM	Dichloromethane
Diamine	4,9-dioxa-1,12-dodecanediamine
DMAP	4-dimethylaminopyridine
FE	Eutrophication, freshwater
FU	Functional unit
FWT	Ecotoxicity, freshwater
GHG	Greenhouse gas
GLO	Dataset refers to global worldwide relevant data
HT-c	Human toxicity, cancer
HT-nc	Human toxicity, non-cancer
ILCD	International Life Cycle Data System
IR	Ionizing radiation
LCA	Life cycle assessment
LCI	Life cycle inventory
LU	Land use
MC6	5-((allyloxy)methyl)-5-ethyl-1,3-dioxan-2-one
ME	Eutrophication, marine

MeOK	Potassium methoxide
<i>m</i> -XDA	<i>m</i> -xylylenediamine
NIPU	Non-isocyanate polyurethane
ODP	Ozone depletion
P	Phosphorus
PHU	Polyhydroxyurethane
PM	Particulate matter
PM2.5	Particles with a diameter of less than 2.5 µm
POF	Photochemical ozone formation
PU	Polyurethane
RER	Datasets refer to Europe-relevant data
RES-f	Resource use, fossils
RES-m	Resource use, minerals and metals
RoW	Rest-of-World-relevant data
SI	Supplementary Information
TE	Eutrophication, terrestrial
TEBAC	Benzyltriethylammonium chloride
THF	Tetrahydrofuran
TMPAE	Trimethylolpropane allyl ether
TMPTC	Trimethylolpropane triglycidyl carbonate
TMPTGE	Trimethylolpropane triglycidyl ether
TMPTM	Trimethylolpropane tris(3-mercaptoproionate)
TriC6	2-ethyl-2-(((3-((5-ethyl-2-oxo-1,3-dioxan-5-yl)methoxy)propyl)thio)propanoyl)oxy)me-thyl)propane-1,3-diyl bis(3-((3-((5-ethyl-2-oxo-1,3-dioxan-5-yl)methoxy)propyl)thio)propanoate)
VOC	Volatile organic compound
WAT	Water use
5CC	Five-membered cyclic carbonate
6CC	Six-membered cyclic carbonate

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