Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2023, **25**, 4350

Environmental, cost, and chemical hazards of using alternative green solvents for fullerene (C_{60}) purification†

Seyed M. Heidari, Eunsang Lee, Ben Cecil and Annick Anctil *

C_{60} is a nanomaterial produced from the pyrolysis of hydrocarbons that needs to be extracted and purified to obtain the desired properties. Previous studies reported purification as the environmental hotspot of the C_{60} production process. However, no study has evaluated existing C_{60} purification methods and proposed alternatives based on environmental, cost, and chemical hazards. Here we used life cycle assessment (LCA) and evaluated the most common existing C_{60} purification methods (chromatography-crystallization, crystallization, & complexation) and identified selective complexation with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the greenest existing C_{60} purification technique that has less environmental (70% from chromatography-crystallization & 50% from crystallization), cost (70% from chromatography-crystallization & 80% from crystallization), and chemical (30% from chromatography-crystallization & crystallization) hazards. The solvent (1,2,4-trymethylbenzene (TMB)) was identified as the environmental hotspot contributing to more than 95% of the cumulative energy demand (CED) of the complexation process. We employed green chemistry principles and an iterative approach to assess the performance of potential replacements (linseed oil, olive oil, toluene, & xylene) for TMB. Although we evaluated solvents that are expected to be greener than petroleum-based solvents, we determined toluene as the greenest alternative. Compared to the baseline complexation method, using toluene reduced the environmental impact by 59%, cost by 85%, and chemical hazards by 42%. Identifying toluene as the alternative green solvent for C_{60} purification can reduce the carbon footprint of C_{60}-containing products used for various emerging applications, such as solar cells, hydrogen storage, biofuels, *etc.*, which aligns with current decarbonization strategies.

Received 14th March 2023,
Accepted 9th May 2023

DOI: 10.1039/d3gc00859b

rsc.li/greenchem

1. Introduction

Nanomaterials such as C_{60} require a large volume of solvents and are usually energy intensive to produce.[1] C_{60} is comprised of 60 carbon atoms forming a closed cage carbon molecule, and it has the most stable structure among fullerenes (C_{60}, C_{70}, and $C_{>70}$).[2] C_{60} has been used in various emerging applications, including solar cells,[3] biofuels,[4] hydrogen storage,[5] drug delivery,[6] photodynamic therapy,[7] cosmetic products,[8] and human supplement.[9] The global fullerene market is expected to increase from about 490 million US dollars in 2020 to more than 730 million US dollars by 2027.[10,11] C_{60} is typically synthesized, at an industrial scale, from combusting hydrocarbons at a high temperature and low pressure to produce fullerene-containing soot (Fig. S1 in ESI†).[2] During the separation stage, the fullerene mix that contains C_{60} and higher fullerenes is separated from soot. Finally, purification is necessary to extract C_{60} from the fullerene mix. In a previous study, our group identified purification as the environmental hotspot of C_{60} production due to the quantity of hazardous solvents and energy required to produce high-purity material.[12]

Existing C_{60} purification methods require a large amount of energy and hazardous solvents. There are various methods to purify C_{60}, and the most commons are chromatography, crystallization, and complexation.[13] For chromatography, the difference in chemical affinity of C_{60}, higher fullerenes, and the stationary phase allows the separation of about 50% of C_{60} with 99% purity from higher fullerenes.[14,15] This technique requires a large amount of stationary and mobile phase (*e.g.*, hazardous solvents like hexane), increasing the cost and the risk of hazardous exposure to the environment and workplace.[13,16] For crystallization, the different solubility of C_{60} and higher fullerenes at specific temperatures (*e.g.*, maximum C_{60} solubility at 110 °C for the C_{60}-containing solution and −16 °C for the C_{70}-containing solution) can yield 67%

Department of Civil and Environmental Engineering, Michigan State University, East Lansing, Michigan 48824, United States. E-mail: Heidari1@msu.edu, leeeunsa@msu.edu, cecilben@msu.edu, anctilan@msu.edu

† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d3gc00859b**

separation of C_{60} with 99% purity.[17,18] The main drawback of the crystallization method is a large amount of energy necessary to cool down or warm up the solution, which does not follow the "*design for energy efficiency*" green chemistry principle. A 99% purity cannot be achieved in a single step, so the crystallization process must be repeated.[18] For complexation, due to the higher electron affinity of C_{70} and higher fullerenes compared to C_{60}, a bicyclic amidine, typically 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), can selectively form a complex with C_{70} and higher fullerenes sooner than C_{60}, resulting in separating about 76% of C_{60} with 99% purity.[19,20] However, similar to the other purification methods, this process needs a large volume of hazardous solvents, which can increase the cost and the carbon footprint of C_{60}-containing products.

There is a need to evaluate and reduce the environmental, cost, and chemical hazards of C_{60} purification. The only comparison of C_{60} purification methods used only purification yield as the indicator of "environment-friendly" process,[13] which is a misleading method since (1) there is no environmental evaluation (*e.g.*, global warming potential (GWP), cumulative energy demand (CED), & water demand (WD) impact assessment) reported for purification methods and (2) C_{60} production rates and solvents' life-cycle environmental, cost, and chemical hazards are ignored while these are vital to compare purification methods, identify the greenest existing purification method, and determine greener replacements. An alternative method to evaluate chemical process sustainability was previously developed by our group and used to evaluate the existing process and help identify greener synthesis methods.[21] The method combines process-based life cycle assessment (LCA) and green chemistry to evaluate the environmental, chemical hazard, and cost impacts of the existing chemical process, and the green chemistry principles are used to identify alternative processes. In this work, we used the same method to evaluate existing C_{60} purification methods (chromatography-crystallization, crystallization, & complexation) and identified the best initial method to be complexation (baseline). To further reduce the environmental impacts of the process of the baseline method, the iterative approach was repeated until an alternative process was identified that simultaneously reduced the environmental, cost, and chemical hazards compared to the baseline. This study shows the significance of conducting LCA to identify alternative processes, as the perceived "greener" alternatives are not always better. The proposed alternative purification process is cheaper, which can benefit C_{60} medical and industrial consumers, and has lower environmental impacts (*e.g.*, GWP), which would help industry meet their GHG emission reduction targets.

2. Materials and methods

2.1. Sustainability assessment

The sustainability methodology to evaluate and guide fine chemical synthesis was developed by our group previously.[21] The method combines process-based life cycle assessment (LCA) and green chemistry to evaluate the impacts of chemical synthesis and identify concerns in the production process. The functional unit is to purify one kg of C_{60} with 99% purity. The production process was evaluated on the basis of environmental, chemical, and cost to identify the hotspots. Green chemistry was employed to determine greener replacements for the hotspots. The iterative approach was repeated until an alternative process was identified that simultaneously reduced the environmental, cost, and chemical hazards compared to the baseline. LCA was conducted using SimaPro 9.1.0.7[22] to quantify the environmental impacts (GWP, CED, WD) of purifying 1 kg of C_{60} with 99% purity. The environmental evalu-

Seyed M. Heidari

Dr Seyed Mohammadreza Heidari is a Postdoctoral Research Fellow at the University of Michigan working on Circular Material Economy. He received his Ph.D. in Environmental Engineering under the supervision of Professor Annick Anctil at Michigan State University, where they conducted this study. Contact email: seyedmheidari[at] gmail.com.

Eunsang Lee

Dr Eunsang Lee is an environmental scientist focusing on life cycle assessment (LCA), sustainability, and corporate carbon management. After completing his Ph.D. dissertation in 2018 under the supervision of Dr Annick Anctil at Michigan State University, he joined the Institute for Environmental Science and Policy at the University of Illinois at Chicago, where he worked as a post-doctoral research associate. His Ph.D. work was centered on assessing organic photovoltaic materials by utilization of LCA and green chemistry, and his current research interests range from sustainable semiconductor technologies to corporate carbon management.

ation was based on data collected from Ecoinvent 3.3, US-EI from DATA SMART, published articles (Table S2†), and experiments. *E*-factor, the ratio of waste mass per product mass, was also used for calculating environmental scores (eqn (1)). We considered the most common environmental impacts (GWP & CED); however, this study could be expanded by considering other ecological factors in future work. The cost and chemical hazard evaluation was conducted based on our previous paper.[21] In summary, chemical hazard analysis was based on NFPA 704 standard scores, including health, flammability, reactivity, and special hazards[23] (eqn (2) and (3)). Cost assessment was based on the production rate of the target substrate and the life cycle cost (LCC) of required raw materials (eqn (4)). These values were normalized using the values of the baseline process, then averaged into a single cost metric value for analysis.

$$\mathrm{ES_i} = \frac{\left(\frac{\mathrm{GWP_i}}{\mathrm{GWP_B}} + \frac{\mathrm{CED_i}}{\mathrm{CED_B}} + \frac{\mathrm{WD_i}}{\mathrm{WD_B}} + \frac{E\text{-factor}_\mathrm{i}}{E\text{-factor}_\mathrm{B}}\right) \times 100}{4} \tag{1}$$

where $\mathrm{ES_i}$ is the environmental score of purification processes i, and B shows the environmental impacts of the baseline process.

$$\mathrm{HS_i} = \frac{\sum_{j=1}^{n} (\mathrm{HM}_j \times \mathrm{AM}_j)}{\sum_{j=1}^{m} (\mathrm{HM}_{j\mathrm{B}} \times \mathrm{AM}_{j\mathrm{B}})} \times 100 \tag{2}$$

$$\mathrm{HM}_j = \frac{\mathrm{Health}_j + \mathrm{Flammability}_j + 0.5(\mathrm{Reactivity}_j + \mathrm{Special}_j)}{3} \tag{3}$$

where $\mathrm{HS_i}$ is the chemical hazard score of the purification process i, n is the number of solvents used in the purification process i, HM_j is the chemical hazard of solvent j based on NFPA 704 standard scores, AM_j is the volume of solvent j, m is the number of solvents used in the baseline process, $\mathrm{HM}_{j\mathrm{B}}$ & $\mathrm{AM}_{j\mathrm{B}}$ are the chemical hazards and the volume of solvents used in the baseline.

$$\mathrm{CS_i} = \frac{\left(\frac{\mathrm{PR_i}}{\mathrm{PR_B}} \times 100\right) + \left(\frac{\sum_{j=1}^{n} (\alpha_j \times \beta_j)}{\sum_{j=1}^{m} (\alpha_{j\mathrm{B}} \times \beta_{j\mathrm{B}})} \times 100\right)}{2} \tag{4}$$

where $\mathrm{CS_i}$ is the cost score of purification process i, $\mathrm{PR_i}$ is the production rate for process i, $\mathrm{PR_B}$ is the baseline production rate, n is the number of primary energy sources used in the process i, αj is the amount of primary energy, βj is the price per unit of primary energy, and B represents values for the baseline process.

2.1.1. Green chemistry principles. Green chemistry principles are described in Table S1.†[24] This study identified alternative solvents with high C_{60} solubility (to reduce the volume of required solvents – principle #5) and lower toxicity (to reduce the risk of accidental release and avoid toxifying the final products – principles #4 & #12). Plant-based solvents were also considered in this study in accordance with principle #7, which is about using renewable feedstock. We used lethal concentration 50 (LC_{50} – a concentration that can cause 50% death in an experimental animal population exposed to a toxicant during a predetermined period[25]) to indicate solvent toxicity and identify potential alternatives for the baseline solvent. LC_{50} can be calculated from toxicity experiments or estimated using software such as the Toxicity Estimation Software Tool (TEST, V5.1.[26] TEST was developed by the U.S. Environmental Protection Agency (EPA) to allow users to estimate the LC_{50} of some chemicals based on molecular structures. For petroleum-based solvents (*e.g.*, toluene and xylene), we used TEST to calculate LC_{50}, and for plant-based solvents (olive oil and linseed oil), we used LC_{50} from our previous work.[27]

2.2. Fullerene C_{60} purification

2.2.1. Materials. All chemicals were used as received. Fullerene mix (70% C_{60}, 29% C_{70}, and 1% higher fullerenes)

Ben Cecil

Benjamin J. Cecil received his BSc. in Chemistry at Northern Kentucky University and performed graduate work in Sustainability at Michigan State University. He now works as a Project Scientist at Nitto Avecia supporting the development and manufacture of Oligonucleotides used to treat a variety of diseases through genetic medicine platforms.

Annick Anctil

Dr Annick Anctil is an Associate Professor in Civil and Environmental Engineering at Michigan State University, where she leads research on Sustainable Energy Systems. She holds a BE and MS in Materials Engineering and a PhD in Sustainability. She uses proactive sustainability assessment to reduce the environmental impact of new technologies. At MSU, she teaches classes on sustainability and life cycle assessment of energy.

was purchased from SES Research Group (Houston, TX), C_{60} and C_{70} with +99% purity from MER (Tuscan, AZ), 1,2,4-trimethylbenzene (TMB) CAS 95636 (+98%), toluene CAS 108883 (ACS reagent, +99.5%), xylenes CAS 1330207 (ACS reagent, +98.5%), linseed oil CAS 8001261 (MQ200), olive oil CAS 8001250 (MQ200, highly refined), hexane CAS 110543 (HPLC grade, +85% *n*-hexane), 2-propanol CAS 67630 (HPLC grade, 99.9%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) CAS 6674222 (puriss., +99% GC), 2-methyltetrahydrofuran CAS 96479 (+99%), were purchased from Sigma Aldrich Burlington, MA.

2.2.2. **Complexation process.** The C_{60} purification process was based on previous studies.[20,28] In summary, the fullerene mix, including C_{60}, C_{70}, and higher fullerenes, was dissolved in five mL of TMB using an ultrasonic bath for five min at room temperature. The complexation process started by adding 103 µl of DBU and four µl of DI water in 10 min while the solution was continuously mixed at a low speed to avoid a vortex. The complexation continued under the nitrogen atmosphere for five hours to let DBU, C_{70}, and higher fullerenes form a solid complex. A 0.2-micron filter was used to separate the complex containing C_{70} and higher fullerenes from the solution containing C_{60}. The remaining DBU was removed using 0.2 M acetic acid. Isopropanol was used to separate C_{60} particles from the solution *via* a 24-hours crystallization process. Finally, C_{60} particles were collected and dried to remove the residual solvent.

We used the iterative method described in 2.1 to modify the baseline process (Fig. 1). As shown in Fig. 1, the material produced from the baseline process was characterized, and screening was used based on C_{60} purity and yield and sustainability evaluation of potential alternative procedures with a comparable purity and yield to the baseline. The best alternative purification process was identified based on environmental, cost, and chemical hazards. High-performance liquid chromatography (HPLC-UV) was used to measure C_{60} purity.[29–33] The column was YMC-Pack ODS-A™ (5 µm, 120 Å, 150 × 6 mm I.D.), the mobile phase was hexane/2-propanol (70/30), the flow rate was 0.7 mL min^{-1}, the wavelength was 350 nm (0.08 AUFS), and injection was four µL.[34]

3. Results and discussion

3.1. Baseline selection

The first step was to select a baseline among existing methods (chromatography-crystallization,[35] crystallization,[36] and complexation[20]) based on the lowest environmental, cost, and chemical hazard scores. Fig. 2A shows the process flow diagram of the complexation and the system boundary used for sustainability assessment. Similar figures are available in the ESI† for chromatography-crystallization and crystallization methods (Fig. S2 and S3†). The environmental score of the complexation was two times lower than crystallization and three times lower than chromatography-crystallization (Fig. 2C). The GWP of the complexation was also six to ten times lower than the two other approaches. The CED to purify one kg of C_{60} with 99% purity was 7340 MJ for the complexation and increased to 12 900 MJ per kg-C_{60} for crystallization and 22 500 MJ per kg-C_{60} for chromatography-crystallization. The higher CED for the crystallization methods is due to the use of the large volume of solvents in the liquid chromatography for pretreatment in the chromatography-crystallization purification method. We observed a similar trend for WD. The WD of complexation was seven times lower than the crystallization and 50 times less than chromatography-crystallization. The chemical hazard scores, which vary from zero to four, were 1.0 for complexation, 1.4 for crystallization, and 1.6 for chromatography-crystallization. The purification rate was seven and 11 times higher for complexation than the other two processes. However, the complexation's Life Cycle Cost (LCC) was between the other two methods. Fig. 2C shows that complexation had the lowest environmental, chemical, and chemical hazard scores. Therefore, we identified the complexation method as the baseline.

3.2. Baseline evaluation

The next step was to identify the environmental hotspots of the baseline. Fig. 3 shows the CED for the complexation process, which includes all processing stages to obtain 99% purity C_{60}. The system boundary and details about the complexation process are shown in Fig. 2A. The solvent, TMB, contributed to more than 95% of the total CED of the baseline purification process since the CED of TMB is high (70 MJ kg^{-1}) and large volume is used. Therefore, TMB was determined as the environmental hotspot, and the following steps focused on identifying alternatives to reduce the environmental burden of C_{60} purification.

3.3. Alternative solvents for TMB

After identifying TMB as the environmental hotspot for the baseline, the next step was to explore alternative greener and nontoxic solvents. We used the C_{60} solubility and toxicity score to identify alternative solvents in accordance with the following green chemistry principles (Table S1† - #3: use substances with no or little toxicity, #4: design safer chemicals with lower environmental toxicity, #5: use less solvents, #7: use renewable feedstocks, and #12: safer substrates for accident prevention). Fig. 4 shows the toxicity scores and the solubility of C_{60} in various solvents. The purple area identifies solvents with a lower toxicity score than TMB and comparable C_{60} solubility to TMB. Two groups of solvents were selected as potential replacements: plant-based and petroleum-based solvents. Linseed and olive oil were chosen since they are nontoxic,[27] have a higher solubility than TMB, and are extracted from renewable feedstocks. Xylene and toluene were selected because they are also less toxic than TMB and have comparable C_{60} solubility to TMB. The normalized toxicity score was 0.24 for TMB, 0.17 for xylene, 0.12 for toluene, 0.12×10^{-3} for linseed oil, and 0.38×10^{-4} for olive oil. The normalized solubility score was 0.34 for TMB, 0.18 for xylene, 0.16 for toluene, 1.0 for linseed oil, and 0.44 for olive oil. Fig. 4A presents detailed information on solvent toxicity scores and C_{60} solubility.

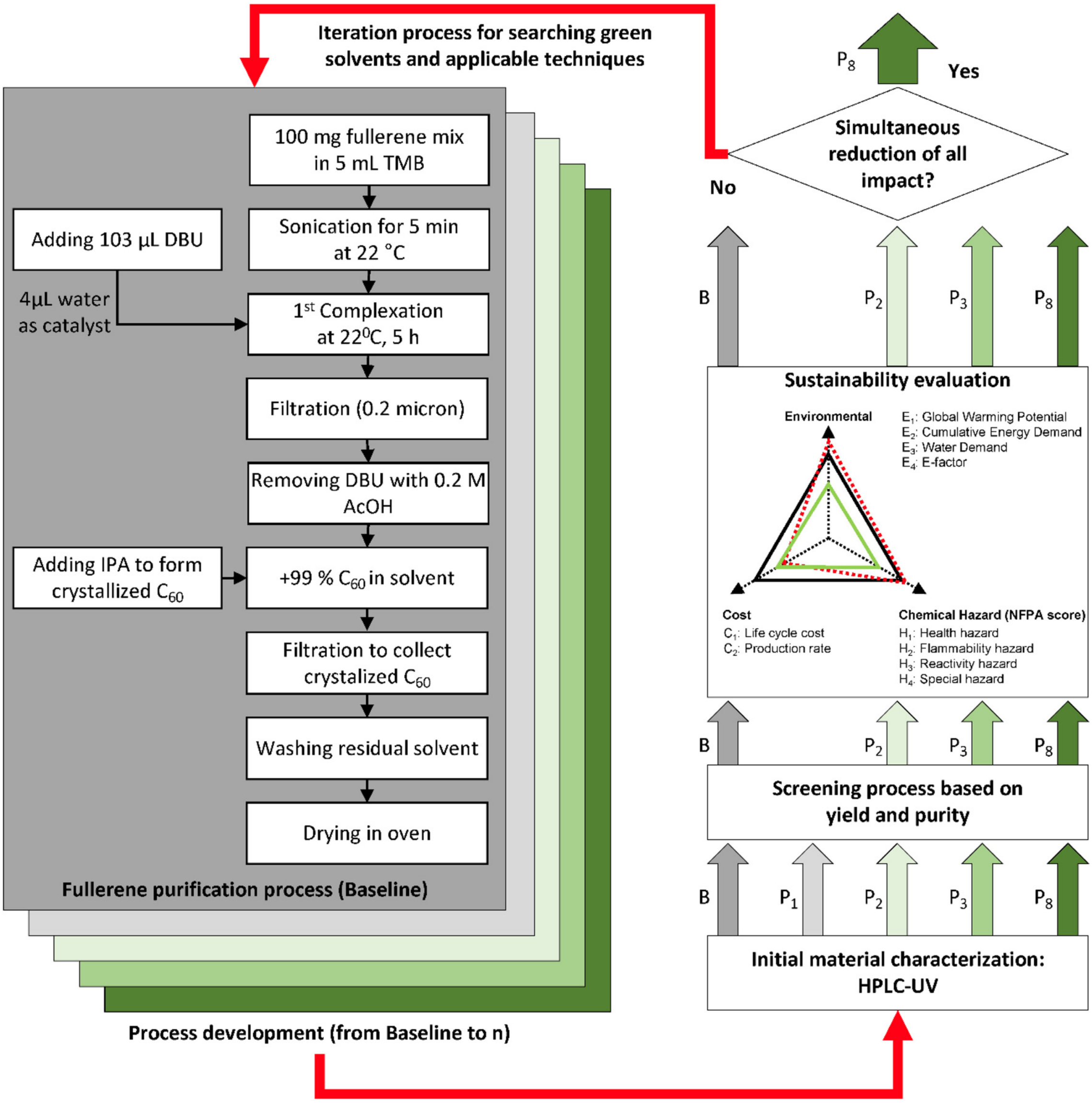
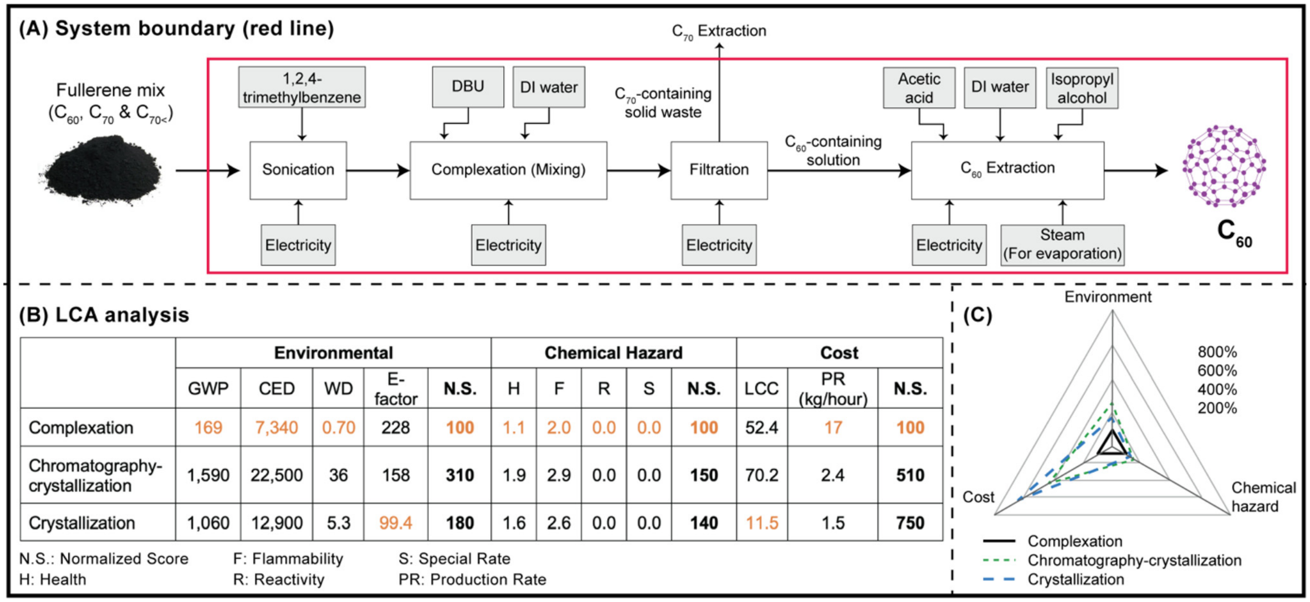


Fig. 1 The experimental approach to identify alternative C_{60} purification methods for the baseline process.

Many green solvents are considered "environment-friendly" based only on the environmental impact of the solvent production stages.[37] However, the environmental benefit of green solvents should also consider their performance in a specific application and the impact of recycling or disposal of the solvent. A typical example of a green solvent with varying benefits is water, which requires a large amount of energy if it needs to be removed using evaporation. In this case, linseed oil has a higher solubility and a lower toxicity score than TMB (Fig. 4B), making it a good candidate for medical applications where C_{60} and linseed oil can behave as drug carriers to treat target cancer cells. But for purification, where the solvent needs to be removed, the high boiling point of linseed oil is a concern. A high boiling point means more energy consumption is necessary for solvent regeneration, which might increase the products' environmental effects. However, this depends on the overall performance of the target solvent. Therefore, this work considered both the upstream environmental impact of manufacturing the solvent and the use of the solvent for purification and compared it with TMB.

3.4. Fullerene purification

3.4.1. Modified baseline process. We modified the baseline process before evaluating the performance of potential TMB replacements for C_{60} purification. This modification was conducted to reduce the environmental impacts of the experimental starting point. The baseline purification yield was about 44%, where a considerable portion of C_{60} was lost due to the non-efficient filtration method. A centrifuge was used to overcome the issue and improve the yield. Centrifuges might consume more energy than pumps used in the filtration process; however, higher efficiency can save more materials for



	Environmental					Chemical Hazard					Cost		
	GWP	CED	WD	E-factor	**N.S.**	H	F	R	S	**N.S.**	LCC	PR (kg/hour)	**N.S.**
Complexation	169	7,340	0.70	228	**100**	1.1	2.0	0.0	0.0	**100**	52.4	17	**100**
Chromatography-crystallization	1,590	22,500	36	158	**310**	1.9	2.9	0.0	0.0	**150**	70.2	2.4	**510**
Crystallization	1,060	12,900	5.3	99.4	**180**	1.6	2.6	0.0	0.0	**140**	11.5	1.5	**750**

N.S.: Normalized Score
H: Health
F: Flammability
R: Reactivity
S: Special Rate
PR: Production Rate

Fig. 2 (A) The LCA system boundary for the complexation process. Grey boxes show input chemicals/energy. (B) The LCA results of existing C_{60} purification methods. Normalized scores (N.S.) are bold, and favorable numbers for sustainability are in orange. (C) The environmental, cost, and chemical hazards of existing C_{60} purification methods to determine the baseline (the process with the lowest impacts is given a score of 100%). GWP: Global Warming Potential, CED: Cumulative Energy Demand, WD: Water Demand, LCC: Life Cycle Cost, DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene.

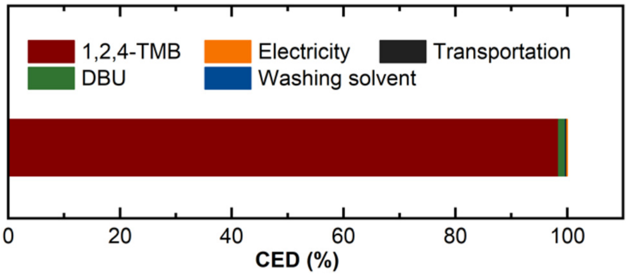
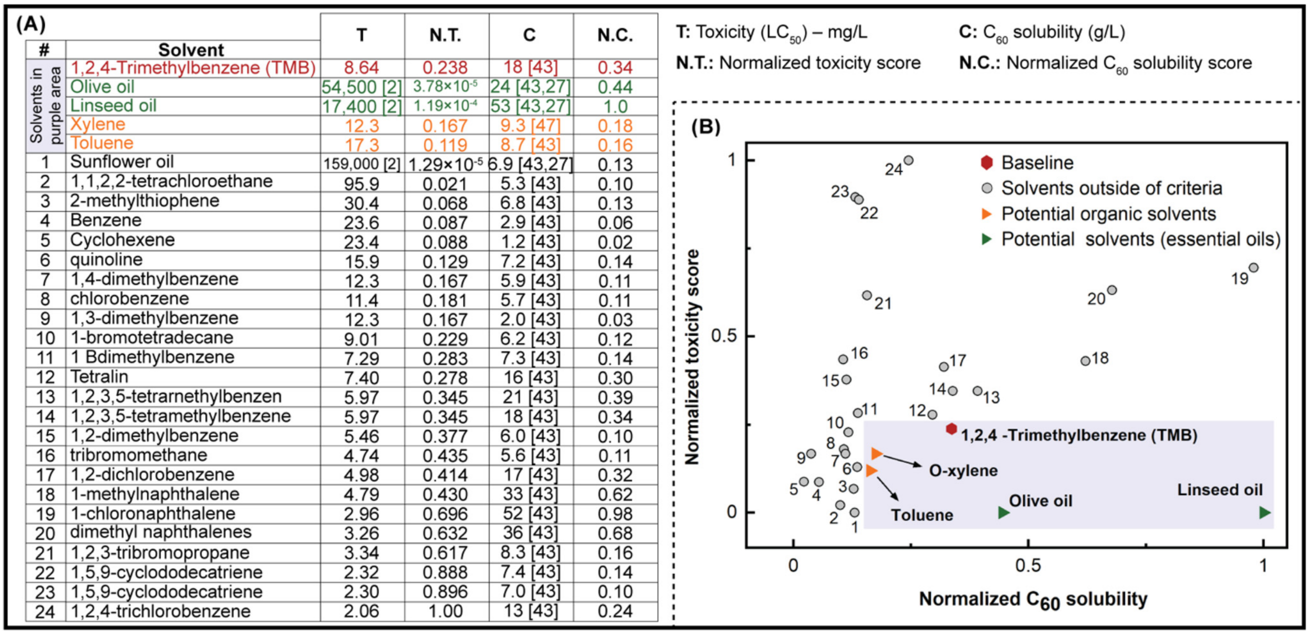


Fig. 3 Cumulative energy demand (CED) for the purification of one kg C_{60} with 99% purity (cradle to gate) using complexation with DBU.

high-energy intensive materials like C_{60}, consequently reducing the overall energy of the material production. In this modified baseline, the purification yield increased to 76%, resulting in fewer environmental, cost, and chemical hazard impacts. The modified baseline had about 43% less environmental and chemical hazard impacts and was 22% cheaper than the baseline. We conducted more experiments to reduce the modified baseline's environmental, cost, and chemical hazards.

3.4.2. Alternative plant-based solvents (P_1 to P_6). After modifying the baseline, we employed potential alternative solvents for C_{60} purification. Linseed and olive oil were chosen as plant-based replacements for TMB because they are less toxic. This is in harmony with green chemistry principles #3: use substances with no or little toxicity, #4: design safer chemicals with lower environmental toxicity, and #12: safer substrates for accident prevention. Plus, linseed and olive oil have a higher C_{60} solubility than TMB, favoring green chemistry principle #5: design to use less solvents. Both oils are extracted from renewable feedstocks, following green chemistry principle #7: use renewable feedstocks (see Table S1† for the complete list of green chemistry principles).

The challenge of using linseed and olive oil for C_{60} purification was identifying a practical approach for dissolving C_{60}. Various methods were evaluated to dissolve fullerenes in linseed oil and olive oil. In P_1, fullerene was dissolved in olive oil, stirring for 72 h at room temperature under a nitrogen atmosphere (since C_{60} reacts with oxygen quickly[38]), as was suggested by Cataldo *et al.*[39] C_{60} purification yield was lower than 5% because the fullerene-mix particles were not fully dissolved in olive oil at the beginning of the experiment, and complexation might only occur at the surface. In this situation, C_{70} and higher fullerenes could not form a solid complex with DBU during the complexation. As mentioned earlier, C_{60} is highly energy-intensive; therefore, C_{60} purification yield can tremendously influence the environmental impacts of C_{60}-made products. So, it was necessary to increase the purification yield. In P_2, the fullerene mix was added to olive oil at 75 °C. At the same time, the solution was stirred for two hours under a nitrogen atmosphere, as Cataldo *et al.*[40] The purification yield was still lower than 5% since the oil might have been decomposed and reacted with C_{60} at a high temperature. P_3 was based on a suggestion to use a sonication bath for 15 min at 50 °C to dissolve fullerenes in olive oil.[41–43] The purification yield increased to 26%, which was much higher than P_1 and P_2 but still lower than the modified baseline purifi-



#	Solvent	T	N.T.	C	N.C.
Solvents in purple area	1,2,4-Trimethylbenzene (TMB)	8.64	0.238	18 [43]	0.34
	Olive oil	54,500 [2]	3.78×10^{-5}	24 [43,27]	0.44
	Linseed oil	17,400 [2]	1.19×10^{-4}	53 [43,27]	1.0
	Xylene	12.3	0.167	9.3 [47]	0.18
	Toluene	17.3	0.119	8.7 [43]	0.16
1	Sunflower oil	159,000 [2]	1.29×10^{-5}	6.9 [43,27]	0.13
2	1,1,2,2-tetrachloroethane	95.9	0.021	5.3 [43]	0.10
3	2-methylthiophene	30.4	0.068	6.8 [43]	0.13
4	Benzene	23.6	0.087	2.9 [43]	0.06
5	Cyclohexene	23.4	0.088	1.2 [43]	0.02
6	quinoline	15.9	0.129	7.2 [43]	0.14
7	1,4-dimethylbenzene	12.3	0.167	5.9 [43]	0.11
8	chlorobenzene	11.4	0.181	5.7 [43]	0.11
9	1,3-dimethylbenzene	12.3	0.167	2.0 [43]	0.03
10	1-bromotetradecane	9.01	0.229	6.2 [43]	0.12
11	1 Bdimethylbenzene	7.29	0.283	7.3 [43]	0.14
12	Tetralin	7.40	0.278	16 [43]	0.30
13	1,2,3,5-tetrarnethylbenzen	5.97	0.345	21 [43]	0.39
14	1,2,3,5-tetramethylbenzene	5.97	0.345	18 [43]	0.34
15	1,2-dimethylbenzene	5.46	0.377	6.0 [43]	0.10
16	tribromomethane	4.74	0.435	5.6 [43]	0.11
17	1,2-dichlorobenzene	4.98	0.414	17 [43]	0.32
18	1-methylnaphthalene	4.79	0.430	33 [43]	0.62
19	1-chloronaphthalene	2.96	0.696	52 [43]	0.98
20	dimethyl naphthalenes	3.26	0.632	36 [43]	0.68
21	1,2,3-tribromopropane	3.34	0.617	8.3 [43]	0.16
22	1,5,9-cyclododecatriene	2.32	0.888	7.4 [43]	0.14
23	1,5,9-cyclododecatriene	2.30	0.896	7.0 [43]	0.10
24	1,2,4-trichlorobenzene	2.06	1.00	13 [43]	0.24

Fig. 4 (A) Solvent toxicity scores and C_{60} solubility. (B) The normalized toxicity and C_{60} solubility score of solvents are used to identify replacements for TMB. The purple area highlights potential alternative solvents.

cation yield. In P_4, we replaced the sonication bath with an ultrasonic probe to improve the amount of dissolved C_{60} in olive oil before the complexation. 100 mg of the fullerene mix was dissolved in four mL of olive oil using the ultrasonic probe for three minutes while the container remained in a water bath to keep the temperature close to room temperature. This resulted in a 44% C_{60} purification yield. Fig. S4† shows the system boundary and process flow of P_4.

Similar approaches were used to dissolve C_{60} in linseed oil. P_5 and P_6 were to identify the best purification yield for the purification method using linseed oil instead of TMB. In P_5, we dissolved 100 mg of the fullerene mix in two mL of linseed oil using an ultrasonic bath for 15 min at 55 °C, as was recommended in the literature.[41–43] The purification yield was 36%. P_6 was based on using the ultrasonic probe for three minutes at room temperature. The purification yield increased to 61% for P_6. Fig. S5† shows the system boundary and process flow of P_6. We considered P_3 & P_4 for olive oil and P_5 & P_6 for linseed oil life cycle environmental assessments.

3.4.3. Alternative petroleum-based solvents (P_7 & P_8). Besides the plant-based solvents (linseed & olive oil), two petroleum-based solvents (toluene and xylene) were among the potential replacements for the baseline solvent (TMB) (Fig. 4B). Toluene and xylene were selected due to their high C_{60} solubility (in accordance with green chemistry principle #5: design to use less solvents) and low toxicity score compared to TMB (#3: use substances with no or little toxicity, #4: design safer chemicals with lower environmental toxicity, and #12: safer substrates for accident prevention) (Fig. 4). We dissolved 100 mg of the fullerene mix in 7.5 mL of xylene in P_7 and eight mL of toluene in P_8. The rest of the procedures were similar to the modified baseline. The C_{60} purification yield was 70% for P_7 and 77% for P_8. Fig. S6 and S7† illustrate the process flow and the system boundary used for the life cycle environmental evaluation of P_7 and P_8. Fig. S8–S10† show the HPLC-UV analysis of the baseline and alternative purification processes.

3.5. Environmental, cost, and chemical hazard evaluation of potential replacements

Process-based environmental, cost, and chemical hazard assessments were needed to determine greener replacements. Selected petroleum-based solvents are more toxic than plant-based solvents and have a lower C_{60} solubility; however, solvent performance in the purification process can significantly affect environmental evaluations. For example, olive oil C_{60} solubility is higher than TMB C_{60} solubility, which reduces the amount of solvent needed to dissolve C_{60} at the beginning of purification. However, more solvent is necessary to separate C_{60} from C_{60}-containing solution along the process, which can influence the purification process's overall environmental, cost, and chemical hazard burden. Therefore, it was necessary to consider a process-based LCA to quantify the environmental, cost, and chemical hazards of potential purification processes to identify greener alternative solvents.

3.5.1. Environmental impact assessment. The C_{60} purification process using toluene (P_8) had the lowest environmental impacts (GWP, CED, WD, and *E*-factor). Table 1 presents the LCA details for the baseline, the modified baseline, and alternative purification methods (P_{3-8}). The modified baseline had about 57% less environmental impact than the baseline because a higher purification yield than the baseline resulted in using less chemicals for producing one kg of C_{60}. C_{60} purifi-

Table 1 Environmental analysis of purification processes – from red to brown, yellow, and green: approaching environmentally benign

Methods	CED (MJ)	Normalized CED	GWP (kg CO_2 eq.)	Normalized GWP	WD (m^3)	Normalized WD	*E*-factor	Normalized *E*-factor	Normalized environmental score
Baseline	8950	100	308	100	9.0	100	381	100	100
Modified baseline	5110	57.1	176	57.1	5.0	56	217	57	57
P_3	30 100	337	1790	581	94	1040	1090	290	567
P_4	28 300	316	1710	554	88	1003	816	210	522
P_5	15 400	172	823	267	33	370	641	170	244
P_6	6770	75.6	348	113	13	147	325	85	105
P_7	3180	35.5	195	63.3	9.0	102	46.5	12	53
P_8	2510	28.0	151	49.0	7.0	78	39.9	10.0	41

cation with olive oil (P_3 and P_4) had the highest environmental impact score, almost five times higher than the baseline and ten times higher than the modified baseline. Olive oil production requires energy, water, and chemicals, increasing associated environmental impacts. Olive oil is obtained from the fruit of olive trees, which requires irrigation at the growing stage, followed by crushing and pressing stages to produce olive paste before oil extraction,[44] increasing energy consumption. Another reason is that a large quantity of solvent (*e.g.*, heptane) is necessary to extract C_{60} from a C_{60}-containing solution compared to the amount of IPA required in the baseline and the modified baseline, which increase the olive oil C_{60} purification's environmental burden.

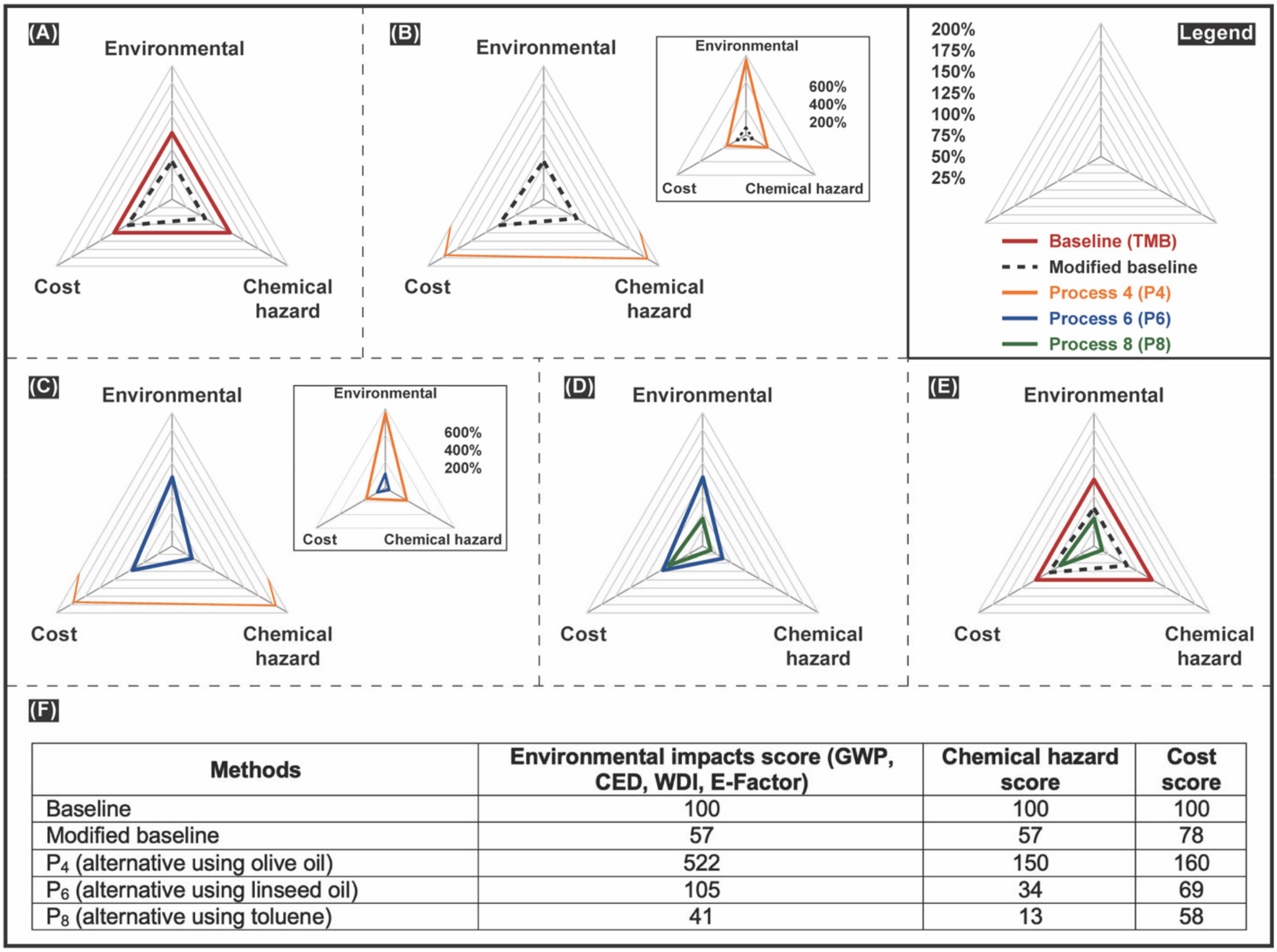
C_{60} purification with linseed oil (P_5 and P_6) had lower environmental impacts than purification with olive oil but had higher environmental impacts than the modified baseline. Linseed oil C_{60} solubility is higher than olive oil C_{60} solubility, decreasing the needed solvent for C_{60} purification. Also, linseed oil is obtained from flax seed, which consumes less water than olive trees at the growing stages. Plus, there is no need for crushing and pressing flax seeds to obtain linseed oil, as these are necessary for olive oil production. Therefore, less energy and water are needed upstream of linseed oil C_{60} purification than olive oil C_{60} purification. Another important reason was that the C_{60} purification process yield was about 17% higher for linseed oil, influencing the purification environmental impacts. C_{60} purification with xylene (P_7) had lower environmental impacts than purification with olive oil, linseed oil, the baseline, and the modified baseline. C_{60} purification with toluene (P_8) had the lowest environmental impacts compared to the baseline, modified baseline, and other alternative methods. This is because the C_{60} purification process yield is highest for toluene, and toluene can be regenerated, consuming less chemicals and energy necessary for C_{60} purification. The environmental impact score of C_{60} purification with toluene was about 60% less than the baseline and 28% less than the modified baseline.

3.5.2. Cost assessment. The C_{60} purification process using toluene (P_8) had the lowest cost impact. Tables 2 and S3, S4† show the life cycle cost analysis and the purification rate of the baseline and alternative methods, including P_{3-8}. It was found that the process with the highest cost metric compared to the baseline was the process that used olive oil as the purification solvent. This is due to the high-cost burden of the chemicals necessary for the olive oil process, as the production rate is comparable to that of the baseline and other processes. Due to the high-cost burden associated with using TMB in the baseline process, all studied processes had lower cost metrics than olive oil-based ones. The processes with the lowest comparative cost metric were the xylene and toluene-based, owing to their low cost of production from crude oil sources.

Table 2 Cost metric values and chemical hazard scores of processes

Method	Cost metric value	Hazard score for all used chemicals
Baseline	100	100
Modified baseline	77.8	57
P_3 (alternative using olive oil)	162	190
P_4 (alternative using olive oil)	160.0	150
P_5 (alternative using linseed oil)	97.0	74
P_6 (alternative using linseed oil)	69.1	34
P_7 (alternative using xylene)	61.2	15
P_8 (alternative using toluene)	58.4	13

3.5.3. Chemical hazard assessment. Chemical hazard impacts were quantified for potential alternative solvents as well as alternative purification methods. The chemical hazard score of solvents was 1.3 for TMB, 2.0 for toluene and xylene, 0.33 for linseed oil, and 0.67 for olive oil. The chemical hazard score of alternative purification processes was calculated according to the amount of chemicals used in each process. Table 2 shows normalized chemical hazard process scores to the baseline. The modified baseline chemical hazard score was 57. The highest chemical hazard score was 190 for the purification method using olive oil (P_3). This is because more chemicals were necessary for C_{60} purification; therefore, more chemicals were counted for chemical hazard assessment. The chemical hazard score was 34 for the method using linseed oil (P_6). It was almost six times lower than the chemical hazard score of P_3 since less amount of solvent was required due to the higher C_{60} solubility of linseed oil. The chemical hazard score was even lower for the alternative methods using petroleum-based solvents mostly because toluene and xylene can be regenerated; therefore, less quantity of solvents contributed to chemical hazard evaluation. The lowest chemical hazard score was 13 for the purification process using toluene instead



Methods	Environmental impacts score (GWP, CED, WDI, E-Factor)	Chemical hazard score	Cost score
Baseline	100	100	100
Modified baseline	57	57	78
P_4 (alternative using olive oil)	522	150	160
P_6 (alternative using linseed oil)	105	34	69
P_8 (alternative using toluene)	41	13	58

Fig. 5 The environmental, cost, and chemical hazard evaluation of (A) the baseline and the modified baseline, (B) P_4 (olive oil), (C) P_6 (linseed oil), (D) P_8 (toluene) for C_{60} purification. (E) A comparison of the baseline, the modified baseline, and the best alternative process (P_8). (F) The details of environmental, cost, and chemical hazards of C_{60} purification.

of TMB. Table S5† presents the detailed calculation of the solvent's chemical hazard scores.

3.6. Overall evaluation

The overall evaluation of C_{60} purification processes showed that the C_{60} purification process using toluene had the lowest scores and therefore was identified as a green replacement for C_{60} purification. Fig. 5 summarizes the environmental, cost, and chemical hazards evaluation of the baseline, the modified baseline, and potential alternative methods (P_{3-8}) for C_{60} purification. Linseed and olive oil are nontoxic solvents with high C_{60} solubility extracted from renewable feedstocks, and these are in harmony with green chemistry principles #3, #4, #7, and #12. However, the process-based life cycle analysis showed that the total impacts of C_{60} purification were lower for toluene than linseed and olive oil. This was due to the large amount of energy, water, and chemicals necessary for producing olive oil and linseed oil. Also, the C_{60} purification yield was lower for purification methods using olive oil and linseed oil, which increased the amount of chemicals necessary for making one kg of C_{60}. Another reason was that linseed and olive oil have a higher boiling point (570–590 K) compared to toluene (383 K) and xylene (417 K), which increased the energy necessary for solvent regeneration, and all linseed and olive oil were counted in process-based life cycle evaluations. Due to these reasons and overall process-based life cycle evaluations, toluene performed greener than other solvents and was determined as the green replacement for TMB for C_{60} purification. The purification efficiency for the baseline process (TMB) was 44%, and for the alternative process (Toluene) was 77%. Fig. S8 and S10† show the properties of C_{60} purified in the baseline process (TMB) and the alternative method (Toluene). Our results highlight the importance of conducting LCA to identify alternative processes, as the perceived "greener" alternatives are not always better.

Identifying solutions to reduce the environmental impacts of chemical production processes and, more importantly, the environmental burden of using chemicals in various applications is essential to address global environmental challenges such as climate change. The Intergovernmental Panel on

Climate Change (IPCC) recently pointed out that more ambitious climate action plans are necessary to achieve the expected reduction of GHG emission goals by 2050,[45] and many governments have established ambitious goals to address this issue. In the US, one example of a GHG reduction policy is the GHG Emission Reduction Plan by 2030,[46] which relies on modifying current processes with high GHG emissions and developing alternatives with less and zero emissions. In this regard, chemicals can play an essential role in maximizing the environmental benefits of these replacements or, on the other side, add a new environmental burden. The GHG emissions of the chemical industry contribute to about 10% of total US manufacturing GHG emissions and have increased by 8% from 2012 to 2021 and reached more than 186 million metric tons of CO_{2eq}.[47,48] So, it is vital to carefully investigate the process-based environmental impacts of using chemicals and chemical production to reach the GHG emission reduction goals.

Chemicals can influence the environment upstream and downstream. The upstream impacts can be mainly due to chemical production, such as toluene from petroleum, olive oil from olive trees, *etc*. The downstream effects are due to, for instance, the use of chemicals in various applications. For example, the toluene performance in the C_{60} purification process to provide C_{60} needed for cosmetic products can generate environmental effects due to the co-chemicals necessary for C_{60} purification. This causes selecting green chemicals (*e.g.*, greener solvents) more complex since, besides the chemical production procedure, the implication of chemicals in target processes can also enormously contribute to the impacts. Plus, each chemical may act and behave differently depending on the purpose of its usage. Therefore, choosing proper tools to determine greener replacements for environmental hotspots (*e.g.*, toxic solvents) based on direct and indirect effects is vital to be more following environmental impact reduction efforts. Employing LCA and green chemistry for chemical decision-making is also emphasized for a better environmental evaluation in another published work.[49] As we previously showed[21] and further explained in this study, an iterative approach can help with solvent selection since green chemistry researchers can investigate using in-process monitoring to assess essential parameters such as process yields and conduct process-based sustainability evaluation to ensure the alternative "green" alternative does not create unintended environmental, cost and chemical hazards.

4. Conclusion

C_{60} is a highly energy-intensive material used in many emerging technologies and applications, including perovskite solar cells, hydrogen storage, biofuels, cosmetic products, and human supplement. We aimed to maximize material use efficiency and minimize environmental, cost, and chemical hazards of C_{60} purification to reduce the environmental burden of C_{60}-containing products. We identified selective complexation with DBU as the greenest existing method to purify C_{60} with 99% purity. Our further environmental evaluations showed that the baseline solvent (TMB) was the environmental hotspot and contributed to more than 95% of the cumulative energy demand. Therefore, we identified olive oil, linseed oil, xylene, and toluene as potential alternative solvents for TMB as they were less toxic and had a comparable C_{60} solubility to TMB, which were in accordance with green chemistry principles.

This study showed that the performance of the potential alternative solvents for purifying C_{60} influenced the green solvent selection procedure. We used an iterative approach to evaluate the replacements' performance and employed a process-based life cycle assessment to evaluate potential alternative C_{60} purification process sustainability. Linseed and olive oil are both nontoxic and have a higher C_{60} solubility than TMB, xylene, and toluene. However, plant-based oil production requires more energy, water, and chemicals than xylene and toluene at the solvent production stage and along the C_{60} purification process. Furthermore, some solvents require additives and process modifications to perform similarly or better than the baseline solvent. As an example, olive oil is a non-toxic solvent. Still, more heptane is necessary to separate C_{60} from C_{60}-containing solution compared to what is required in the baseline, which results in a higher environmental, cost, and chemical hazard score.

This study employed green chemistry principles and process-based LCA to determine green solvents for C_{60} purification, which can reduce the environmental impacts (*e.g.*, GWP, CED, WD, & *E*-factor) of many products containing C_{60}. This approach can be applied to many other fine chemicals, which are more likely energy-intensive than bulk materials. Evaluating the fundamental physicochemical properties of host–guest interactions in the presence of plant-based oils was not the scope of this study; however, further research might be insightful to assess the overall performance of plant-based oils as potential green solvents in the chemical production industry.

Abbreviations & parameters

CED	Cumulative energy demand
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
GHG	Greenhouse gas
GWP	Global warming potential
HPLC	High-performance liquid chromatography
IPA	Isopropyl alcohol
IPCC	Intergovernmental panel on climate change
LCA	Life cycle assessment
LCC	Life cycle cost
LC_{50}	Lethal concentration 50
NFPA	National fire protection association
P_1	Process #1
P_n	Process #*n*
TEST	Toxicity estimation software tool

TMB	1,2,4-Trymethylbenzene
WD	Water demand
K	Kelvin
AM_j	The volume of solvent j
AM_{jB}	The volume of solvents used in the baseline
CS_i	The cost score of the purification process i
ES_i	The chemical hazard score of the purification process i
HS_i	The chemical hazard score of the process i
HM_j	The chemical hazard score of solvent j
HM_{jB}	The chemical hazard of solvents used in the baseline
PR_i	The production rate for process i
PR_B	The baseline production rate
αj	The amount of primary energy
βj	The price/unit of primary energy
B	Represents values for the baseline process

Author contributions

Seyed M. Heidari: conceptualization, formal analysis, investigation, methodology, validation, visualization, writing (original draft, review & editing). Eunsang Lee: conceptualization, formal analysis for existing C_{60} purification methods, methodology, validation, writing (review & editing). Ben Cecil: formal analysis (LCC of alternative methods), writing (review). Annick Anctil: conceptualization, funding acquisition, resources, supervision, methodology, validation, writing (review & editing).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This material is based upon work supported by National Science Foundation under Grant NSF-1511098 and NSF-1801785.

References

1 H. C. Kim and V. Fthenakis, Life cycle energy and climate change implications of nanotechnologies: A Critical Review, *J. Ind. Ecol.*, 2013, 528–541.

2 H. Takehara, M. Fujiwara, M. Arikawa, M. D. Diener and J. M. Alford, Experimental study of industrial scale fullerene production by combustion synthesis, *Carbon*, 2005, **43**(2), 311–319.

3 T. Gatti, E. Menna, M. Meneghetti, M. Maggini, A. Petrozza and F. Lamberti, The Renaissance of fullerenes with perovskite solar cells, *Nano Energy*, 2017, **41**, 84–100.

4 A. Y. Pulyalina, A. A. Larkina, M. V. Tataurov, L. V. Vinogradova and G. A. Polotskaya, Hybrid macromolecular stars with fullerene (C60) core included in polyphenyleneisophthalamide membranes for n-butanol dehydration, *Fullerenes, Nanotubes Carbon Nanostruct.*, 2020, **28**(1), 54–60.

5 J. Joseph, V. S. Sivasankarapillai, S. Nikazar, M. S. Shanawaz, A. Rahdar, H. Lin, *et al.*, Borophene and Boron Fullerene Materials in Hydrogen Storage: Opportunities and Challenges, *ChemSusChem*, 2020, **13**(15), 3754–3765.

6 M. Kumar and K. Raza, C60-fullerenes as Drug Delivery Carriers for Anticancer Agents: Promises and Hurdles, *Pharm. Nanotechnol.*, 2018, **5**(3), 169–179.

7 S. M. Heidari and M. Golsorkhi, Fullerene (C_{60}) Evaluation for Photodynamic Therapy, *NDDTE Conference Proceedings*, 2020.

8 H. Zhou, D. Luo, D. Chen, X. Tan, X. Bai, Z. Liu, *et al.*, Current Advances of Nanocarrier Technology-Based Active Cosmetic Ingredients for Beauty Applications, *Clin., Cosmet. Invest. Dermatol.*, 2021, (14), 867–887.

9 SES Research Group, C_{60} in Olive oil, **https://www.sesres.com/carbon-60-olive-oil/**(accessed 1 Dec 2019).

10 Emergen Research, Fullerene Market By Type (C_{60}, C_{70}, C_{76}, Other), By Production Method (Arc Discharge Method, CVD/CCVD Process, Laser Ablation of Graphite, Others), By Shape (Nanotubes, Bucky Balls, Nano-Rods), By End-use, and By Region Forecast to 2028, **https://www.emergenresearch.com/industry-report/fullerene-market** (accessed 4 July 2022).

11 Maximize Market Research, Global fullerene Market (2021 to 2027) – Growth, Trends, COVID-19 Impact and Forecasts, **https://www.maximizemarketresearch.com/market-report/global-fullerenes-market/70582/**(accessed 4 July 2022).

12 A. Anctil, C. W. Babbitt, R. P. Raffaelle and B. J. Landi, Material and energy intensity of fullerene production, *Environ. Sci. Technol.*, 2011, **45**(6), 2353–2359.

13 H. Yi, G. Zeng, C. Lai, D. Huang, L. Tang, J. Gong, *et al.*, Environment-friendly fullerene separation methods, *Chem. Eng. J.*, 2017, **330**, 134–145.

14 P. M. Allemand, A. Koch, F. Wudl, Y. Rubin, F. Diederich, M. M. Alvarez, *et al.*, Two different fullerenes have the same cyclic voltammetry, *J. Am. Chem. Soc.*, 1991, **113**(4), 1050–1051.

15 H. Keypour, M. Noroozi and A. Rashidi, An improved method for the purification of fullerene from fullerene soot with activated carbon, celite, and silica gel stationary phases, *J. Nanostruct. Chem.*, 2013, **3**(1), 45.

16 B. A. Khan, L. Cheng, A. A. Khan and H. Ahmed, Healthcare waste management in Asian developing countries: A mini review, *Waste Manage. Res.*, 2019, **37**(9), 863–875.

17 T. Odagiri, Y. C. Chan, K. S. Kwok and K. M. Ng, A novel evaporative crystallization column for the purification of fullerene C_{60}, *AIChE J.*, 2007, **53**(2), 531–534.

18 K. S. Kwok, Y. C. Chan, K. M. Ng and C. Wibowo, Separation of fullerenes C_{60} and C_{70} using a crystallization-based process, *AIChE J.*, 2009, **56**(7), 1801–1812.

19 K. Nagata, E. Dejima, Y. Kikuchi and M. Hashiguchi, Kilogram-scale [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with 1,8-

Diazabicyclo[5.4.0]undec-7-ene (DBU), *Chem. Lett.*, 2005, **34**(2), 178–179.

20 K. Nagata, E. Dejima, Y. Kikuchi and M. Hashiguchi, Efficient and Scalable Method for [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with DBU in the Presence of Water, *Org. Process Res. Dev.*, 2005, **9**(5), 660–662.

21 E. Lee, C. J. Andrews and A. Anctil, An Iterative Approach to Evaluate and Guide Fine Chemical Processes: An Example from Chloroaluminum Phthalocyanine for Photovoltaic Applications, *ACS Sustainable Chem. Eng.*, 2018, **6**(7), 8230–8237.

22 PRé Consultants, SimaPro 9.1.0.7, Amersfoort, **https://pre-sustainability.com/solutions/tools/simapro/**.

23 NFP Association, *NFPA 704: Standard System for the Identification of the Hazards of Materials for Emergency Response*, National Fire Protection Agency, Quincy, MA, 2013 edn, 2011, Harvard.

24 P. G. Jessop, S. Trakhtenberg and J. Warner, *The Twelve Principles of Green Chemistry, Innovations in Industrial and Engineering Chemistry*, American Chemical Society, 2008, pp. 401–436.

25 U.S. EPA, *Fact Sheet - LC50*, 2018, **https://www.epa.gov/sites/default/files/2016-09/documents/ethylene-oxide.pdf** (accessed 17 Octobere 2022).

26 US Environmental Ptotection Agency (EPA), Toxicity Estimation Software Tool (TEST), **https://www.epa.gov/chemical-research/toxicity-estimation-software-tool-test**.

27 S. M. Heidari and A. Anctil, Identifying alternative solvents for C_{60} manufacturing using singular and combined toxicity assessments, *J. Hazard. Mater.*, 2020, **393**, 122337.

28 K. Nagata, E. Dejima, Y. Kikuchi and M. Hashiguchi, Kilogram-scale [60]Fullerene Separation from a Fullerene Mixture: Selective Complexation of Fullerenes with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), *Org. Process Res. Dev.*, 2005, **9**(5), 660–662.

29 A. Astefanei, O. Núñez and M. T. Galceran, Characterisation and determination of fullerenes: A critical review, *Anal. Chim. Acta*, 2015, **882**, 1–21.

30 J. Wang, Q. Cai, Y. Fang, T. A. Anderson and G. P. Cobb, Determination of fullerenes (C_{60}) in artificial sediments by liquid chromatography, *Talanta*, 2011, **87**, 35–39.

31 J. M. Treubig and P. R. Brown, Analysis of C_{60} and C_{70} fullerenes using high-performance liquid chromatography-Fourier transform infrared spectroscopy, *J. Chromatogr. A*, 2002, **960**, 135–142.

32 A. Carboni, E. Emke, J. R. Parsons, K. Kalbitz and P. de Voogt, An analytical method for determination of fullerenes and functionalized fullerenes in soils with high performance liquid chromatography and UV detection, *Anal. Chim. Acta*, 2014, **807**, 159–165.

33 J. B. Howard and J. T. McKinnon, *United States Patent*, 5273729, 1993.

34 YMC HPLC Columns Applications Notebook - WA30000, **https://www.waters.com/webassets/cms/library/docs/wa30000.pdf** (accessed 8 Feb 2021).

35 K. S. Kwok, Y. C. Chan, K. M. Ng and C. Wibowo, Separation of fullerenes C_{60} and C_{70} using a crystallization-based process, *AIChE J.*, 2009, **56**(7), 1801–1812.

36 Y. S. Grushko, V. P. Sedov and V. A. Shilin, Technology for manufacture of pure fullerenes C_{60}, C_{70} and a concentrate of higher fullerenes, *Russ. J. Appl. Chem.*, 2007, **80**(3), 448–455.

37 P. G. Jessop, Searching for green solvents, *Green Chem.*, 2011, **13**(6), 1391.

38 M. Wohlers, H. Werner, D. Herein, T. Schedel-Niedrig, A. Bauer and R. Schlögl, Reaction of C_{60} and C_{70} with molecular oxygen, *Synth. Met.*, 1996, **77**(1–3), 299–302.

39 F. Cataldo and T. Da Ros, Medicinal Chemistry and Pharmacological Potential of Fullerenes and Carbon Nanotubes, *Carbon Materials: Chemistry and Physics*, 2008, vol. 1.

40 F. Cataldo and T. Braun, The Solubility of C_{60} Fullerene in Long Chain Fatty Acids Esters, *Fullerenes, Nanotubes Carbon Nanostruct.*, 2007, **15**(5), 331–339.

41 P. Anatol'evich, P. Petrovich, B. Borisovich, M. Ehrik, R. Mikhajlovich and S. Valentinovich, *et al.*, *Fullerene Solution Prepration Method*, RU2283273C2, Russia, 2006.

42 K. N. Semenov, N. A. Charykov, V. I. Namazbaev, N. I. Alekseyev, E. G. Gruzinskaya, V. N. Postnov, *et al.*, Temperature dependence of solubility of light fullerenes in some essential oils, *Fullerenes, Nanotubes Carbon Nanostruct.*, 2011, **19**(3), 225–236.

43 K. N. Semenov, N. A. Charykov, V. A. Keskinov, A. K. Piartman, A. A. Blokhin and A. A. Kopyrin, Solubility of Light Fullerenes in Organic Solvents, *J. Chem. Eng. Data*, 2010, **55**(1), 13–36.

44 A. Thomas, B. Matthäus and H. J. Fiebig, *Fats and Fatty Oils, Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2015, 1–84.

45 The Latest IPCC Report: What is it and why does it matter?, **https://www.nature.org/en-us/what-we-do/our-insights/perspectives/ipcc-report-climate-change/** (accessed 8 July 2022).

46 Fact Sheet: President Biden Sets 2030 Greenhouse Gas Pollution Reduction Target Aimed at Creating Good-Paying Union Jobs and Securing U.S. Leadership on Clean Energy Technologies (Office of the Press Secretary, United States), Whitehouse.Gov, **https://www.whitehouse.gov/briefing-room/statements-releases/2021/04/22/fact-sheet-president-biden-sets-2030-greenhouse-gas-pollution-reduction-target-aimed-at-creating-good-paying-union-jobs-and-securing-u-s-leadership-on-clean-energy-technologies/%0Awhi**.

47 U.S. EPA, Sources of Greenhouse Gas Emissions, **https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions%0A https://www.epa.gov/climatechange/ghgemissions/sources/transportation.html**, (accessed 20 April 2023).

48 U.S. EPA, Greenhouse Gas reporting in the ethylene manufacturing sector, **https://www.epa.gov/trinationalanalysis/greenhouse-gas-reporting-chemical-manufacturing-sector#:** ~:text=The chemical manufacturing sector reported, an 8% 25 increase since 2012, (accessed 20 April 2023).

49 K. M. D. Reyes, K. Bruce and S. Shetranjiwalla, *J. Chem. Educ.*, 2023, **100**, 209–220.