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

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$C_{60}$  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-trimethylbenzene (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.

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### 1. Introduction

Nanomaterials such as  $C_{60}$  require a large volume of solvents and are usually energy intensive to produce.<sup>1</sup>  $C_{60}$  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  $C_{>70}$ ).<sup>2</sup>  $C_{60}$  has been used in various emerging applications, including solar cells,<sup>3</sup> biofuels,<sup>4</sup> hydrogen storage,<sup>5</sup> drug delivery,<sup>6</sup> photodynamic therapy,<sup>7</sup> cosmetic products,<sup>8</sup> and human supplement.<sup>9</sup> 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.<sup>10,11</sup>  $C_{60}$  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†).<sup>2</sup> 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.<sup>12</sup>

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 common are chromatography, crystallization, and complexation.<sup>13</sup> 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.<sup>14,15</sup> 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.<sup>13,16</sup> 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%

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separation of C<sub>60</sub> with 99% purity.<sup>17,18</sup> 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.<sup>18</sup> For complexation, due to the higher electron affinity of C<sub>70</sub> and higher fullerenes compared to C<sub>60</sub>, a bicyclic amidine, typically 1,8-diaza-bicyclo[5.4.0]undec-7-ene (DBU), can selectively form a complex with C<sub>70</sub> and higher fullerenes sooner than C<sub>60</sub>, resulting in separating about 76% of C<sub>60</sub> with 99% purity.<sup>19,20</sup> 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<sub>60</sub>-containing products.

There is a need to evaluate and reduce the environmental, cost, and chemical hazards of C<sub>60</sub> purification. The only comparison of C<sub>60</sub> purification methods used only purification yield as the indicator of “environment-friendly” process,<sup>13</sup> 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<sub>60</sub> 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.<sup>21</sup> 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<sub>60</sub> 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<sub>60</sub> 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.<sup>21</sup> 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<sub>60</sub> 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<sup>22</sup> to quantify the environmental impacts (GWP, CED, WD) of purifying 1 kg of C<sub>60</sub> with 99% purity. The environmental evalua-



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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.<sup>21</sup> In summary, chemical hazard analysis was based on NFPA 704 standard scores, including health, flammability, reactivity, and special hazards<sup>23</sup> (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.

$$ES_i = \frac{\left( \frac{GWP_i}{GWP_B} + \frac{CED_i}{CED_B} + \frac{WD_i}{WD_B} + \frac{E\text{-factor}_i}{E\text{-factor}_B} \right) \times 100}{4} \quad (1)$$

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

$$HS_i = \frac{\sum_{j=1}^n (HM_j \times AM_j)}{\sum_{j=1}^m (HM_{jB} \times AM_{jB})} \times 100 \quad (2)$$

$$HM_j = \frac{\text{Health}_j + \text{Flammability}_j + 0.5(\text{Reactivity}_j + \text{Special}_j)}{3} \quad (3)$$

where  $HS_i$  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,  $HM_{jB}$  &



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$AM_{jB}$  are the chemical hazards and the volume of solvents used in the baseline.

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

where  $CS_i$  is the cost score of purification process  $i$ ,  $PR_i$  is the production rate for process  $i$ ,  $PR_B$  is the baseline production rate,  $n$  is the number of primary energy sources used in the process  $i$ ,  $\alpha_j$  is the amount of primary energy,  $\beta_j$  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.†<sup>24</sup> 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 toxicifying 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<sup>25</sup>) 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).<sup>26</sup> 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.<sup>27</sup>

## 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)



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was purchased from SES Research Group (Houston, TX), C<sub>60</sub> and C<sub>70</sub> 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<sub>60</sub> purification process was based on previous studies.<sup>20,28</sup> In summary, the fullerene mix, including C<sub>60</sub>, C<sub>70</sub>, 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  $\mu$ L of DBU and four  $\mu$ L 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<sub>70</sub>, and higher fullerenes form a solid complex. A 0.2-micron filter was used to separate the complex containing C<sub>70</sub> and higher fullerenes from the solution containing C<sub>60</sub>. The remaining DBU was removed using 0.2 M acetic acid. Isopropanol was used to separate C<sub>60</sub> particles from the solution *via* a 24-hours crystallization process. Finally, C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> purity.<sup>29–33</sup> The column was YMC-Pack ODS-A<sup>TM</sup> (5  $\mu$ m, 120  $\text{\AA}$ , 150  $\times$  6 mm I.D.), the mobile phase was hexane/2-propanol (70/30), the flow rate was 0.7 mL min<sup>-1</sup>, the wavelength was 350 nm (0.08 AUFS), and injection was four  $\mu$ L.<sup>34</sup>

## 3. Results and discussion

### 3.1. Baseline selection

The first step was to select a baseline among existing methods (chromatography-crystallization,<sup>35</sup> crystallization,<sup>36</sup> and complexation<sup>20</sup>) 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<sub>60</sub> with 99% purity was 7340 MJ for the complexation and increased to 12 900 MJ per kg-C<sub>60</sub> for crystallization and 22 500 MJ per kg-C<sub>60</sub> 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<sub>60</sub>. 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<sup>-1</sup>) 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<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> in various solvents. The purple area identifies solvents with a lower toxicity score than TMB and comparable C<sub>60</sub> 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,<sup>27</sup> 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<sub>60</sub> solubility to TMB. The normalized toxicity score was 0.24 for TMB, 0.17 for xylene, 0.12 for toluene, 0.12  $\times$  10<sup>-3</sup> for linseed oil, and 0.38  $\times$  10<sup>-4</sup> 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<sub>60</sub> solubility.



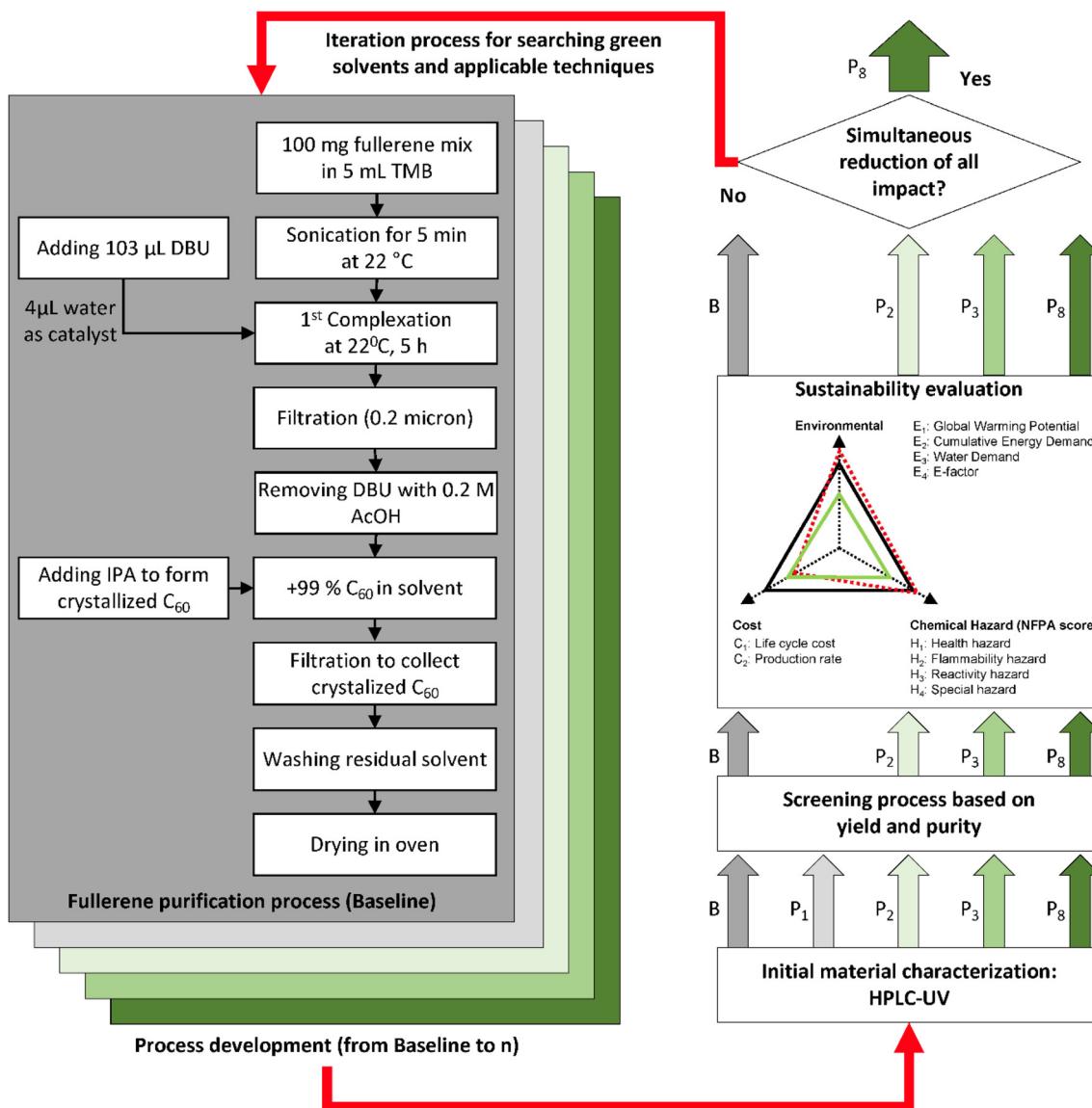


Fig. 1 The experimental approach to identify alternative C<sub>60</sub> purification methods for the baseline process.

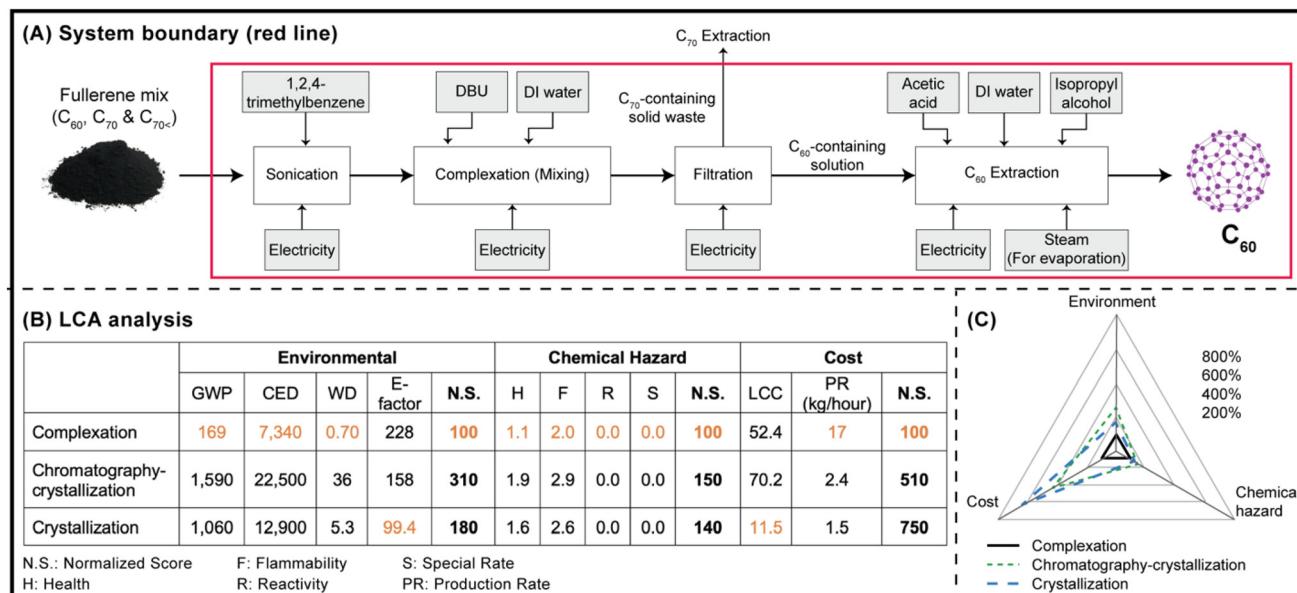
Many green solvents are considered “environment-friendly” based only on the environmental impact of the solvent production stages.<sup>37</sup> However, the environmental benefit of green solvents should also consider their performance in a specific application and the impact of recycling or disposal 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<sub>60</sub> 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.

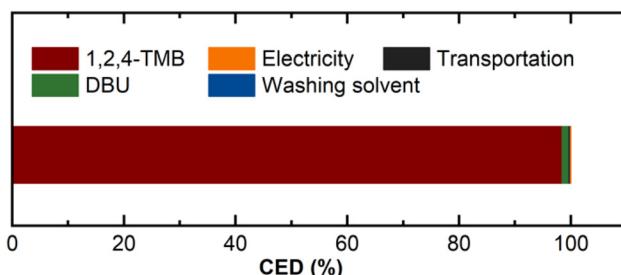
### 3.4. Fullerene purification

**3.4.1. Modified baseline process.** We modified the baseline process before evaluating the performance of potential TMB replacements for C<sub>60</sub> 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<sub>60</sub> 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





**Fig. 2** (A) The LCA system boundary for the complexation process. Grey boxes show input chemicals/energy. (B) The LCA results of existing C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> with 99% purity (cradle to gate) using complexation with DBU.

high-energy intensive materials like C<sub>60</sub>, 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<sub>1</sub> to P<sub>6</sub>).** After modifying the baseline, we employed potential alternative solvents for C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> purification was identifying a practical approach for dissolving C<sub>60</sub>. Various methods were evaluated to dissolve fullerenes in linseed oil and olive oil. In P<sub>1</sub>, fullerene was dissolved in olive oil, stirring for 72 h at room temperature under a nitrogen atmosphere (since C<sub>60</sub> reacts with oxygen quickly<sup>38</sup>), as was suggested by Cataldo *et al.*<sup>39</sup> C<sub>60</sub> 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<sub>70</sub> and higher fullerenes could not form a solid complex with DBU during the complexation. As mentioned earlier, C<sub>60</sub> is highly energy-intensive; therefore, C<sub>60</sub> purification yield can tremendously influence the environmental impacts of C<sub>60</sub>-made products. So, it was necessary to increase the purification yield. In P<sub>2</sub>, 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.*<sup>40</sup> The purification yield was still lower than 5% since the oil might have been decomposed and reacted with C<sub>60</sub> at a high temperature. P<sub>3</sub> was based on a suggestion to use a sonication bath for 15 min at 50 °C to dissolve fullerenes in olive oil.<sup>41–43</sup> The purification yield increased to 26%, which was much higher than P<sub>1</sub> and P<sub>2</sub> but still lower than the modified baseline purifi-

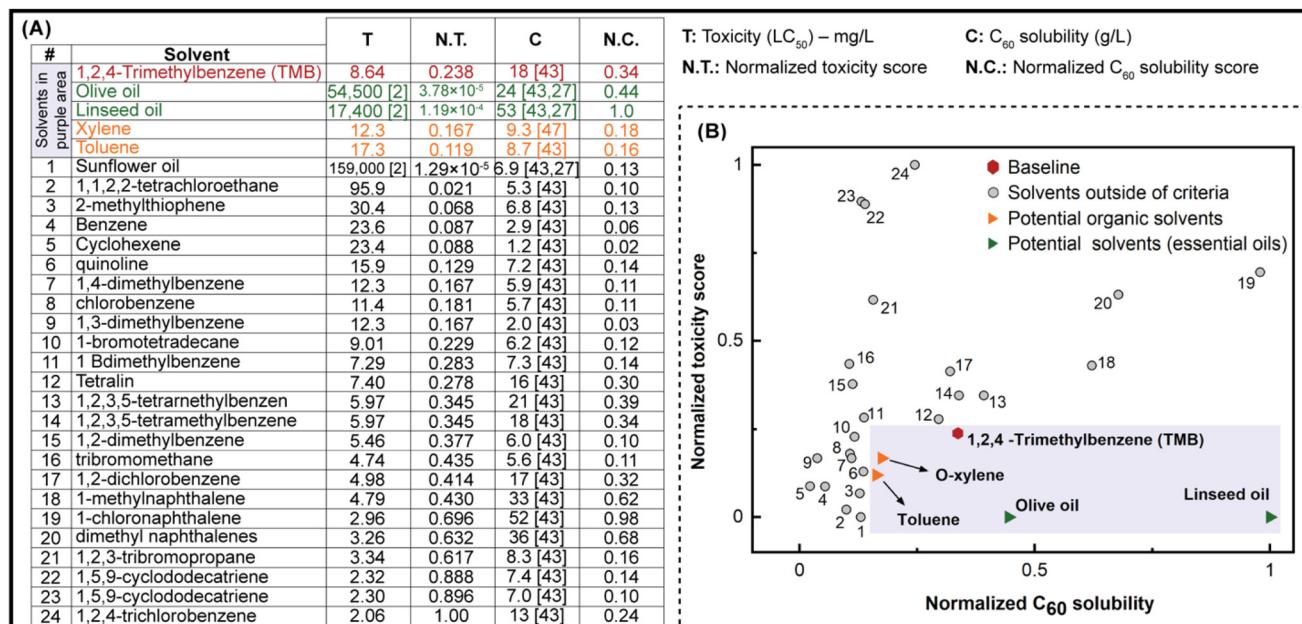


Fig. 4 (A) Solvent toxicity scores and  $C_{60}$  solubility. (B) The normalized toxicity and  $C_{60}$  solubility score of solvents are used to identify replacements for TMB. The purple area highlights potential alternative solvents.

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.<sup>41–43</sup> 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 ( $P_3$ – $P_8$ ). 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 <sub>2</sub> eq.)	Normalized GWP	WD (m <sup>3</sup> )	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 <sub>3</sub>	30 100	337	1790	581	94	1040	1090	290	567
P <sub>4</sub>	28 300	316	1710	554	88	1003	816	210	522
P <sub>5</sub>	15 400	172	823	267	33	370	641	170	244
P <sub>6</sub>	6770	75.6	348	113	13	147	325	85	105
P <sub>7</sub>	3180	35.5	195	63.3	9.0	102	46.5	12	53
P <sub>8</sub>	2510	28.0	151	49.0	7.0	78	39.9	10.0	41

cation with olive oil (P<sub>3</sub> and P<sub>4</sub>) 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,<sup>44</sup> increasing energy consumption. Another reason is that a large quantity of solvent (*e.g.*, heptane) is necessary to extract C<sub>60</sub> from a C<sub>60</sub>-containing solution compared to the amount of IPA required in the baseline and the modified baseline, which increase the olive oil C<sub>60</sub> purification's environmental burden.

C<sub>60</sub> purification with linseed oil (P<sub>5</sub> and P<sub>6</sub>) had lower environmental impacts than purification with olive oil but had higher environmental impacts than the modified baseline. Linseed oil C<sub>60</sub> solubility is higher than olive oil C<sub>60</sub> solubility, decreasing the needed solvent for C<sub>60</sub> 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<sub>60</sub> purification than olive oil C<sub>60</sub> purification. Another important reason was that the C<sub>60</sub> purification process yield was about 17% higher for linseed oil, influencing the purification environmental impacts. C<sub>60</sub> purification with xylene (P<sub>7</sub>) had lower environmental impacts than purification with olive oil, linseed oil, the baseline, and the modified baseline. C<sub>60</sub> purification with toluene (P<sub>8</sub>) had the lowest environmental impacts compared to the baseline, modified baseline, and other alternative methods. This is because the C<sub>60</sub> purification process yield is highest for toluene, and toluene can be regenerated, consuming less chemicals and energy necessary for C<sub>60</sub> purification. The environmental impact score of C<sub>60</sub> purification with toluene was about 60% less than the baseline and 28% less than the modified baseline.

**3.5.2. Cost assessment.** The C<sub>60</sub> purification process using toluene (P<sub>8</sub>) 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<sub>3–8</sub>. 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

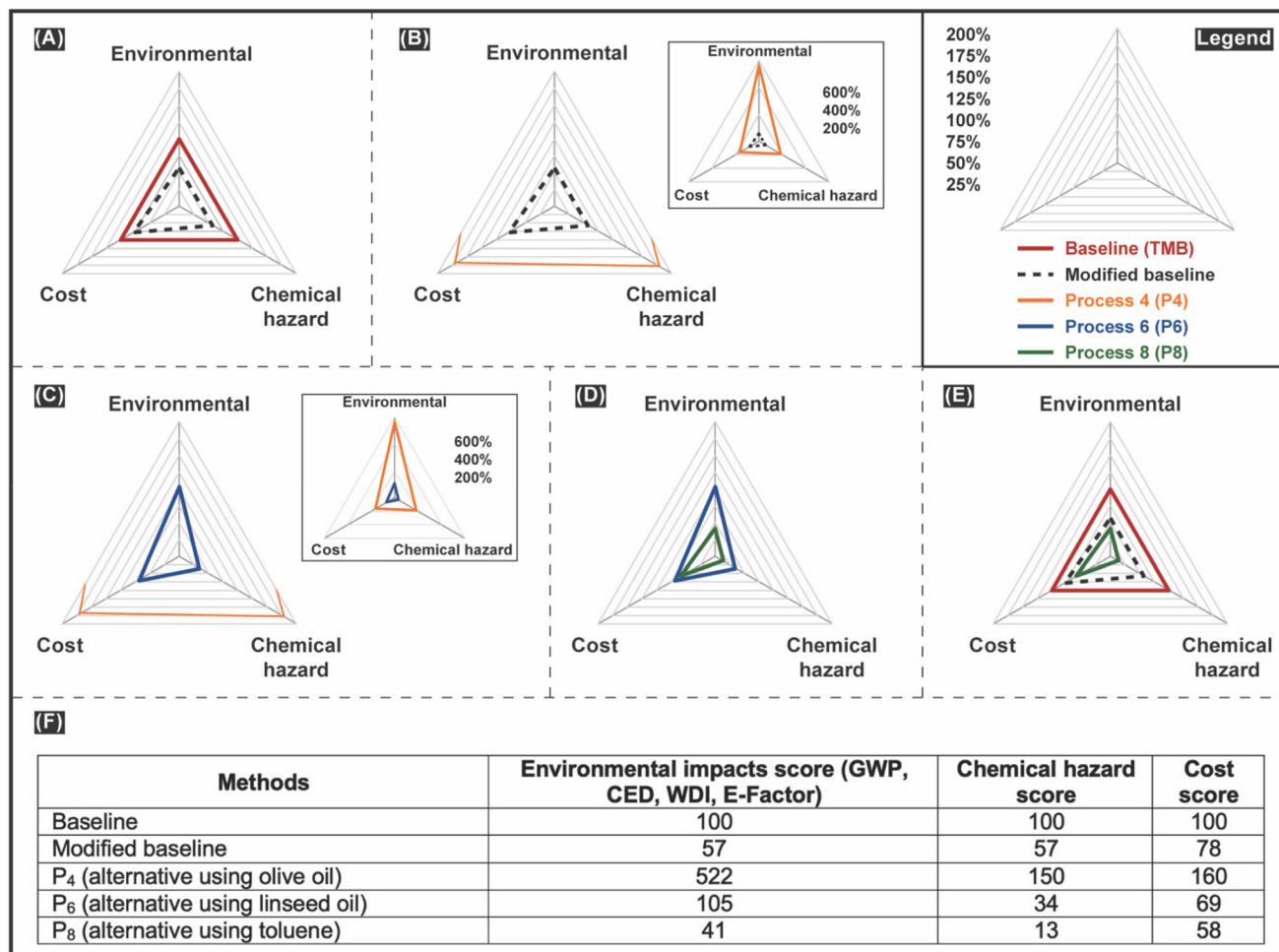
**Table 2** Cost metric values and chemical hazard scores of processes

Method	Cost metric value	Hazard score for all used chemicals
Baseline	100	100
Modified baseline	77.8	57
P <sub>3</sub> (alternative using olive oil)	162	190
P <sub>4</sub> (alternative using olive oil)	160.0	150
P <sub>5</sub> (alternative using linseed oil)	97.0	74
P <sub>6</sub> (alternative using linseed oil)	69.1	34
P <sub>7</sub> (alternative using xylene)	61.2	15
P <sub>8</sub> (alternative using toluene)	58.4	13

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.

**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<sub>3</sub>). This is because more chemicals were necessary for C<sub>60</sub> purification; therefore, more chemicals were counted for chemical hazard assessment. The chemical hazard score was 34 for the method using linseed oil (P<sub>6</sub>). It was almost six times lower than the chemical hazard score of P<sub>3</sub> since less amount of solvent was required due to the higher C<sub>60</sub> 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





**Fig. 5** The environmental, cost, and chemical hazard evaluation of (A) the baseline and the modified baseline, (B) P<sub>4</sub> (olive oil), (C) P<sub>6</sub> (linseed oil), (D) P<sub>8</sub> (toluene) for C<sub>60</sub> purification. (E) A comparison of the baseline, the modified baseline, and the best alternative process (P<sub>8</sub>). (F) The details of environmental, cost, and chemical hazards of C<sub>60</sub> 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<sub>60</sub> purification processes showed that the C<sub>60</sub> purification process using toluene had the lowest scores and therefore was identified as a green replacement for C<sub>60</sub> purification. Fig. 5 summarizes the environmental, cost, and chemical hazards evaluation of the baseline, the modified baseline, and potential alternative methods (P<sub>3-8</sub>) for C<sub>60</sub> purification. Linseed and olive oil are nontoxic solvents with high C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub>. 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<sub>60</sub> 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<sub>60</sub> 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,<sup>45</sup> 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,<sup>46</sup> 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<sub>2eq</sub>.<sup>47,48</sup> 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<sub>60</sub> purification process to provide C<sub>60</sub> needed for cosmetic products can generate environmental effects due to the co-chemicals necessary for C<sub>60</sub> 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.<sup>49</sup> As we previously showed<sup>21</sup> 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<sub>60</sub> 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<sub>60</sub> purification to reduce the environmental burden of C<sub>60</sub>-containing products. We identified selective

complexation with DBU as the greenest existing method to purify C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> purification process sustainability. Linseed and olive oil are both nontoxic and have a higher C<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub> from C<sub>60</sub>-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<sub>60</sub> purification, which can reduce the environmental impacts (*e.g.*, GWP, CED, WD, & *E*-factor) of many products containing C<sub>60</sub>. 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 <sub>50</sub>	Lethal concentration 50
NFPA	National fire protection association
P <sub>1</sub>	Process #1
P <sub>n</sub>	Process #n
TEST	Toxicity estimation software tool



TMB	1,2,4-Trymethylbenzene
WD	Water demand
K	Kelvin
AM <sub>j</sub>	The volume of solvent <i>j</i>
AM <sub>JB</sub>	The volume of solvents used in the baseline
CS <sub>i</sub>	The cost score of the purification process <i>i</i>
ES <sub>i</sub>	The chemical hazard score of the purification process <i>i</i>
HS <sub>i</sub>	The chemical hazard score of the process <i>i</i>
HM <sub>j</sub>	The chemical hazard score of solvent <i>j</i>
HM <sub>JB</sub>	The chemical hazard of solvents used in the baseline
PR <sub>i</sub>	The production rate for process <i>i</i>
PR <sub>B</sub>	The baseline production rate
$\alpha_j$	The amount of primary energy
$\beta_j$	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<sub>60</sub> 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.

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