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# Assessing the environmental impacts of flow and batch syntheses of hypercrosslinked polymers for low-pressure CO<sub>2</sub> adsorption

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## ABSTRACT

The microporosity of hypercrosslinked polymers (HCPs) renders such materials ideal adsorbents for carbon capture. We recently showed that the CO<sub>2</sub>/N<sub>2</sub> selectivity of HCPs synthesised by internal crosslinking of poly- $\alpha,\alpha'$ -dichloro-*p*-xylene (p-DCX) in continuous flow synthesis was 850 % higher than those produced in batch reactions. We hypothesised that this could potentially reduce the amount of HCP adsorbents required for delivering the same carbon capture performances, hence improving the environmental impacts of carbon capture. This was evaluated here where we analysed the environmental impacts of using both batch- and flow-synthesised HCPs for adsorbing 40 mg of CO<sub>2</sub> with the life-cycle assessment method. We also deployed this approach to evaluate HCPs synthesised via post-crosslinking of polystyrene crosslinked with DCX (p-PS-DCX) and externally crosslinking of polystyrene with formaldehyde dimethyl acetal (FDA) crosslinker (p-PS-FDA). Amongst all HCPs studied in this work, the changes in environmental impact of deploying internally crosslinked HCPs for carbon capture were the worst. This was mostly attributed to its low product yield (7 %), which had a larger influence on the environmental impacts than its adsorption performance as verified by sensitivity analysis. To offset the adverse effects of low product yield, the product yield from flow synthesis of HCPs should ideally reach 25 %. By identifying that product yield is key for promoting environmental sustainability in carbon capture using flow-derived HCPs, future work should focus on optimising continuous flow synthesis to deliver ideal product yield. Hypercrosslinked polymers (HCPs) can be deployed adsorbents for carbon capture. Here we hypothesise that one can use HCPs with better CO<sub>2</sub>/N<sub>2</sub> selectivity to deliver the same carbon capture performances, hence improving the environmental impacts of carbon capture. This was evaluated here using batch- and flow-synthesised HCPs via internal, external and post-crosslinking strategies with the life cycle assessment method. The environmental impacts of internally crosslinked HCPs were worst due to a low product yield of 7 %. Sensitivity analyses indicated that this limitation can be overcome when HCP yield from flow synthesis reach 25 %. Future work should focus on optimising continuous flow synthesis to deliver ideal product yield for minimising environmental impacts of deploying HCPs in carbon capture.

## 1. Introduction

Addressing climate change in our lifestyle is no longer a mere suggestion but a mandatory action. Carbon dioxide (CO<sub>2</sub>) is one of the greenhouse gases causing the rise in global temperatures, leading to long-term severe climate change. Many countries have set agendas to reduce CO<sub>2</sub> emissions in the COP26 summit held in Glasgow in 2021. This commitment will affect the strategy for reducing and eliminating industrial-scale CO<sub>2</sub> emissions [1].

Utilising porous adsorbents for low pressure, physisorption of CO<sub>2</sub> is widely studied for carbon capture from emission sources due to their simplicity in operation, mild operating conditions, and low material costs [2]. This approach usually works for post-combustion carbon capture where it relies on direct contact between the flue gas and solid adsorbents in a batch operation, followed by regeneration of adsorbents

for multicycle utilization [3]. Adsorbents studied for such applications include activated carbons [4], metal-organic frameworks [5], and microporous polymers [6] such as hypercrosslinked polymers (HCPs) [7–9]. HCPs can be synthesised from various aromatic building blocks, ranging from simple benzene rings [10] to styrene-based copolymer [11] to macrocyclic compound cucurbiturils [12] via Friedel-Crafts alkylation. HCPs are typically synthesised via three main strategies [13], namely, internal, external, and post-crosslinking. Internal crosslinking is based on the direct polycondensation of aromatic compounds with reactive functional groups such as methyl halide [14], methyl hydroxyl [15], or methyl ether [16]. Post-crosslinking involves a secondary reaction to extensively crosslinking of pre-synthesised polymers [17]. This approach may involve the addition of crosslinker such as  $\alpha,\alpha'$ -dichloro-*p*-xylene (DCX) and 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP) to achieve higher degree of crosslinking. External crosslinking

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is based on crosslinking aromatic building blocks, with an emphasis on the specific use of formaldehyde dimethyl acetal (FDA) as an external crosslinker, also known as ‘knitting strategy’ [18].

The choice of crosslinking strategy can tailor HCP microporosity and their Brunauer-Emmett-Teller (BET) surface areas which consequently impacted CO<sub>2</sub> uptake [13]. The synthesis conditions, including synthesis duration and amount of crosslinker reagents, also had an impact on CO<sub>2</sub> adsorption capacity and its selectivity over other gases [15,19]. Moreover, our recently research revealed that the synthetic method of HCPs, *i.e.*, batch vs. flow synthesis also influenced CO<sub>2</sub> and N<sub>2</sub> adsorption capacities [20]. Unlike most studies that focus on developing novel chemistry approaches to improve the separation performances of HCPs, the novelty and focus of this work is to evaluate how a change in reactor type can influence the environmental impact and sustainability of HCP synthesis – a key characteristic of Industry 5.0. In comparison to internally crosslinked poly-dichloro-*p*-xylene (p-DCX) produced in batch reactors, the superior heat and mass transfer rates offered by continuous flow synthesis enhanced the micropore volume of p-DCX by 570 %, increasing from 0.042 cm<sup>3</sup> g<sup>-1</sup> to 0.281 cm<sup>3</sup> g<sup>-1</sup>, whilst reducing pore widths from 2 to 6 nm to under 2 nm. Consequently, this enhanced CO<sub>2</sub>/N<sub>2</sub> selectivity (calculated using ideal adsorption solution theory (IAST) with a mixture gas comprising CO<sub>2</sub> 85% and 15% N<sub>2</sub>, at 298 K and 1 atm) by 850 %, reaching a value of 71 (Table 1). This steep increase in CO<sub>2</sub>/N<sub>2</sub> selectivity suggested that the amount of HCPs deployed as adsorbents for carbon capture could be reduced significantly if they are produced *via* continuous flow synthesis. This would likely bring environmental benefits as fewer materials are used and produced. However, this could only be validated by quantifying and comparing the environmental impacts of using HCPs produced from both batch and flow synthesis methods for low-pressure carbon capture, with a life-cycle assessment (LCA).

Following ISO 14040 and 14044 standards, a typical LCA consist of four stages [21]. In the first stage of Goal Definition, we need to identify which outcomes from the LCA performance would be useful to answer the question posed. This will establish a functional unit which is a reference description that connects all calculations used in the LCA. The second stage is Scope Definition, where the boundary is mapped. This stage resembles material and energy balances where all input and output elementary flows are shown across the foreground processes, *i.e.*, the main processes in which data are obtained directly from the experiment. The third stage, Inventory Analysis, summarises all elementary flows into a table that is linked to the quantities of consumed components from the background processes, including raw material extraction, chemical synthesis, and electricity generation. These processes typically have their own databases provided by third party organisations. In the final stage of Impact Assessment, an impact calculation method is used to reveal the quantitative impact scores for each impact category where higher scores are typically interpreted as negative environmental impacts on the respective category and lower scores infer to positive environmental impacts [22]. The selection of method should correspond

**Table 1**

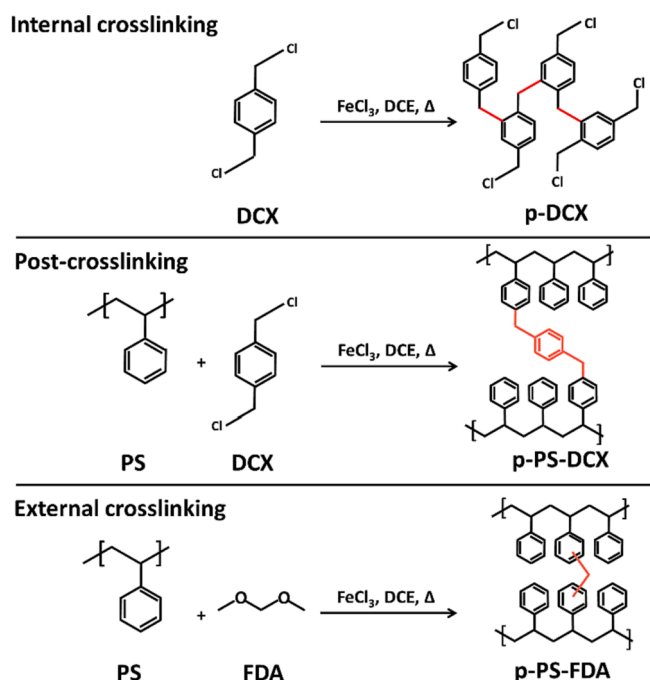
Experimental data of adsorbed pure gas ( $Q_i$ ) at 25 °C, 1 atm by each HCP type together with the calculated gas purity ( $x_i$ ) and CO<sub>2</sub>/N<sub>2</sub> selectivity ( $S_{CO_2/N_2}$ ) at the condition of 25 °C, 1 atm, 15:85 M ratio of inlet flue gas [20].

HCP type	Synthetic approach	Amount of pure gas adsorbed (units)		Calculated gas purity based on IAST (units)		$S_{CO_2/N_2}$
		$Q_{CO_2}$	$Q_{N_2}$	$x_{CO_2}$	$x_{N_2}$	
p-DCX	Batch	0.96	0.26	0.57	0.43	7.5
	Flow	0.93	0.062	0.93	0.074	71
p-PS-DCX	Batch	0.56	0.045	0.78	0.22	20
	Flow	0.42	0.046	0.73	0.27	15
p-PS-FDA	Batch	0.82	0.085	0.81	0.19	25
	Flow	0.56	0.053	0.77	0.23	19

to answering the goal set in the first stage.

A common quantitative basis for evaluating the impact of CO<sub>2</sub> adsorption is using a functional unit related to this process, *i.e.*, the amount of CO<sub>2</sub> adsorbed by the adsorbent such as activated carbon [23], zeolite [24], metal-organic framework [25], and HCPs [26,27]. The key finding from these studies was that the use of different chemicals to synthesise these adsorbents led to different environmental impacts of the same application – carbon capture. For instance, ethylene glycol dimethacrylate-based HCPs that were crosslinked with acrylamide reduced the environmental impact (across four endpoint categories from IMPACT 2002+ method) of carbon capture by 14 – 43 % when compared to the same HCP synthesised from methacrylamide and triallylamine crosslinkers [27]. This trend was also observed in pristine and modified activated carbons yielded from Persian ironwood biomass. Although the CO<sub>2</sub> uptake of modified activated carbon was higher by 2 mmol g<sup>-1</sup>, the environmental burden of this material was 2.5 – 6.7-fold greater for all ten impact categories (CML baseline 2000 method). This was due to the additional consumption of chemicals, especially copper iron (contributed for more than 41.3 % of most impacts except Global warming and Fossil fuel), and electricity (about 43.5 % for Global warming and Fossil fuel categories) during the modification process [23]. Meanwhile, in our previous study, we used a comparative LCA method to determine the environmental impact of deploying flow-synthesised HCPs for dye adsorption [28]. Attributing to the lower dye adsorption capacity of HCPs yielded from flow synthesis, the environmental endpoint impacts of Climate change, Resources, and Human health of flow-synthesised HCPs were more negative than those produced in batch reactions. This was despite that the process of flow synthesis of HCPs had better environmental impacts than batch synthesis. Clearly, adsorbent production plays a key role in influencing the environmental impacts of the final application.

The objective of the current work was to assess and compare the environmental impacts of three HCP types synthesised through batch and flow reactions, with the aim of highlighting the environmental sustainability of the continuous flow system over the batch method. Those reactions based on internal crosslinking (p-DCX), post-crosslinking (p-PS-DCX) and external crosslinking (p-PS-FDA), for utilisation in low pressure CO<sub>2</sub> adsorption (CO<sub>2</sub> 85% and 15% N<sub>2</sub> of inlet flue gas at 298 K and 1 atm). Fig. 1 shows the chemical structures of the



**Fig. 1.** Three synthetic crosslinking approaches for this LCA study.

reagents and their reactions to yield each type of these HCPs. The details of the synthesis procedures for both batch and flow methods, including the calculation of CO<sub>2</sub> and N<sub>2</sub> adsorption and CO<sub>2</sub>/N<sub>2</sub> selectivity could be referred to our previous study [20]. This study followed the same frameworks as the aforementioned standard with a sensitivity analysis at the end of the assessment. The aim was to seek answers for: 1) Do we need lower quantities of flow-synthesised p-DCX for adsorbing the same amount of CO<sub>2</sub> when compared to the same HCP type produced in batch reactions?; 2) If the answer to the first question is yes, will the environmental impacts of carbon capture associated with deploying flow-synthesised p-DCX become lower than those of batch synthesis?

## 2. Experimental section

### 2.1. Goal and scope of the LCA

The goal of this LCA study was to assess how the environmental effects of HCPs deployed for low-pressure CO<sub>2</sub> adsorption would be impacted as a function of production method. The hypothesis was supported by the claim that flow-synthesised internally-crosslinked HCPs offered higher microporosity that consequently enhanced CO<sub>2</sub>/N<sub>2</sub> selectivity; meaning that lower HCP quantities were required. Since less HCPs were needed, the environmental impacts are expected to be lower.

The functional unit of this LCA study was 40 mg of adsorbed CO<sub>2</sub> from the inlet flue gas mixture of 15:85 M ratio of CO<sub>2</sub> and N<sub>2</sub> at 298 K and 1 atm. The reference flows corresponding to the functional unit were the required quantity, *i.e.*, weight of HCPs. These amounts correlated to the adsorption capacities depending on the HCP types and the different synthetic techniques. The required amounts of HCPs were shown in Table 2. The calculation was shown as follows:

$$HCPweight = 40mgCO_2 \times \frac{mmolCO_2}{44mgCO_2} \times \frac{1}{x_{CO_2,purity}} \times \frac{gHCP}{Q_{CO_2,mmolCO_2}}$$

### 2.2. System boundary

The system boundary of this LCA study (Fig. 2) covered upstream production of input components, *i.e.*, chemical production, electricity generation and the HCP synthesis stage. Since the focus of the study was on the effects produced by the HCP batch and flow syntheses, the CO<sub>2</sub> adsorption stage was omitted from the system boundaries. The CO<sub>2</sub> adsorption stage only provided the data for the reference point, *i.e.*, the functional unit for the assessment comparison.

The laboratory experiment, *i.e.*, the synthesis of HCP was conducted at the School of Engineering, the University of Edinburgh, hence, the geological scope of this LCA was determined to be European.

There were several presumptions and constraints related to the system boundary that should be address, shown as following:

- 1) The filtration, washing, and drying stages after the synthesis were omitted from the boundary, as the same protocol and equipment were used for both batch- and flow-synthesised HCPs studied in this work.

**Table 2**  
Required quantities of HCPs for adsorbing 40 mg CO<sub>2</sub>.

HCP types	Crosslinking approach	Required amount of HCPs (g)		Difference of required HCP mass (%)
		Batch synthesis	Flow synthesis	
p-DCX	Internal	1.66	1.06	- 36.3
p-PS-DCX	Post	2.09	2.95	+ 41.0
p-PS-FDA	External	1.37	2.12	+ 55.3

- 2) Hydrogen chloride gas, a by-product of the synthesis of HCP, was considered negligible due to its insignificant amount.
- 3) Cooling water was omitted from the system boundary because the temperature of the inlet and outlet of the cooling water remained unchanged on a laboratory scale, making it recyclable.
- 4) Unreacted substrates were considered part of the waste mixture output, as they fully dissolved in DCE and could not be separate at the end of the process.
- 5) Waste disposal, transportation, and infrastructure were not included in the system due to limitations in data collection.

### 2.3. System modelling

The system was modelled using SimaPro 8.0.3.14. Table 3 contains the experimental data inventory for the foreground process, *i.e.*, the process of HCP synthesis. The data to produce the majority of input flows was obtained fromecoinvent 3 with the exception of missing DCX and FDA data. The DCX data was replaced with 1,4-dichlorobenzene, a chemical with a similar structure [29]. The FDA data, contrarily, was obtained from literature and manually entered [30]. The information on each input flow is shown in the Supplementary Information.

The impact assessment method was IMPACT 2002+ V2.11 [31], where it was reported as 15 midpoint impacts, which could be regrouped into 4 endpoint impacts. Global warming was the only midpoint impact under Climate change endpoint category. Non-renewable energy and Mineral extraction were under Resources endpoint category. Aquatic ecotoxicity, Terrestrial ecotoxicity, Terrestrial acidification/nitrification, Land occupation, Aquatic acidification, and Aquatic eutrophication were grouped under Ecosystem quality. Carcinogens, Non-carcinogens, Respiratory inorganics, Respiratory organics, Ionizing radiation, and Ozone layer depletion were midpoint impacts under Human health endpoint damage. It should be noted that Ozone layer depletion was also considered as Ecosystem quality. However, the impact pathway was still uncertain, hence, it was not included in the current IMPACT 2002+ method.

### 2.4. Sensitivity analysis

We also performed a sensitivity analysis to evaluate how the product yield of flow synthesis affected the environmental impact of deploying such HCPs in low-pressure CO<sub>2</sub> adsorption. The key assumption in this sensitivity analysis was that the quality, *i.e.*, microporosity of such HCPs was consistent, regardless of product yield. Using different hypothetical HCP yields of flow synthesis, we calculated how much input components were needed for synthesising 1.055 g of HCPs to adsorb 40 mg of CO<sub>2</sub>. The inventory table for the sensitivity analysis is available in the Supplementary Information.

## 3. Results and discussion

### 3.1. Impact assessment of HCPs synthesised from batch and flow reactions for carbon capture

The environmental impact of using HCPs synthesised from batch and flow reactions to capture 40 mg of CO<sub>2</sub> were quantified over four endpoint impact categories of Climate change, Resources, Ecosystem quality, and Human health (Fig. 3). Relative increments and reductions in these categories correlate to adverse, and improved environmental impacts, respectively. From Fig. 3, it was clear that regardless of cross-linking strategies, replacing traditional batch reactions with continuous flow reactions to synthesise HCPs reduced the scores for Climate change and Resources. The most significant reductions in these endpoint categories were associated with post-crosslinking (p-PS-DCX), where the scores for Climate change, and Resources were reduced by 70 %, and 62 %, respectively. This trend was also observed with HCPs synthesised from internal (p-DCX) and external crosslinking (p-PS-FDA).

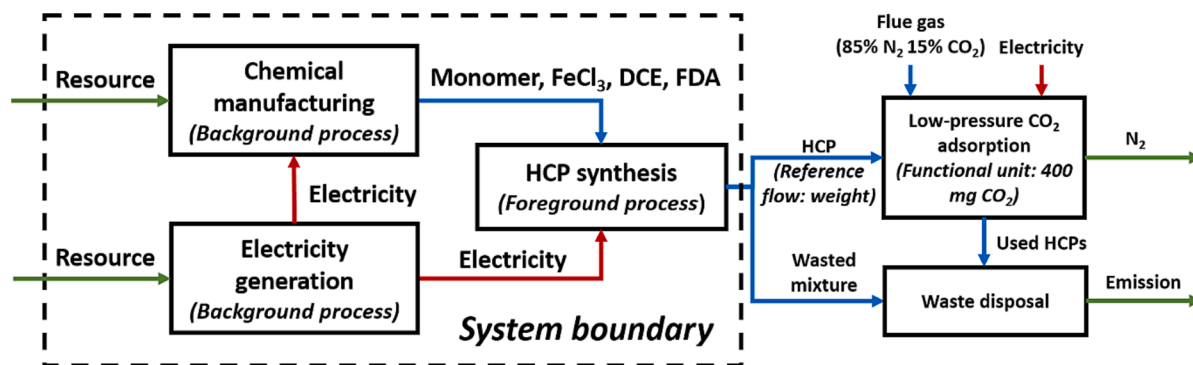


Fig. 2. System boundary of this LCA study as considered partial sections of the life-cycle of HCPs.

Table 3

Inventory of the system for the synthesis of each HCP type via batch and flow reactions.

Components (units)	p-DCX		p-PS-DCX		p-PS-FDA	
	Batch synthesis	Flow synthesis	Batch synthesis	Flow synthesis	Batch synthesis	Flow synthesis
<b>Input</b>						
PS (g)	–	–	1.3	2.3	0.9	1.9
DCX* (g)	2.9	14.6	1.3	2.3	–	–
FDA (g)	–	–	–	–	4.4	9.3
FeCl <sub>3</sub> (g)	2.6	13.5	1.3	2.3	4.4	9.3
DCE (g)	122.6	631.8	437.6	756.5	143.1	304.4
Electricity (kWh)	2.3	0.2	7.0	0.7	2.4	0.5
<b>Output</b>						
HCP** (g)	1.7	1.1	2.1	3.0	1.4	2.1
HCP yield (%)	58.5	7.2	155.3	126.7	156.7	114.3

\* Process input was substituted by the data of 1,4-dichlorobenzene.

\*\* Batch syntheses of all HCPs took place over 24 h, while two batches of p-PS-DCX were required to obtain the required quantity. The required quantities of p-DCX, p-PS-DCX, and p-PS-FDA were obtained after 99, 216, and 141 min *via* flow synthesis.

Surprisingly, the replacement of batch reactions with continuous flow synthesis did not improve Ecosystem quality, where all scores associated with this category, increased by 9 – 197 %. Improvements to the category of Human health was dependent on crosslinking strategy. For example, the use of continuous flow reactions to synthesise post-crosslinked and externally crosslinked HCPs reduced the Human health score by 51 % and 33 %, respectively, when compared to batch reactions. Meanwhile, the use of HCPs synthesised in continuous flow reactions *via* internal crosslinking enhanced the score for Human health by 19 %. By expressing the endpoint impacts as normalised scores, we observed that despite the increments in impact scores across various categories regardless of crosslinking strategies, the overall normalised scores for using HCPs synthesised from batch reactions to capture 40 mg of CO<sub>2</sub> were higher than those from continuous flow reactions, particularly for external and post-crosslinking. In terms of improving environmental impacts, the approach of flow synthesis was more beneficial for external and post-crosslinking. The only benefit for replacing batch reactions with flow synthesis for internal crosslinking was the significant improvements in CO<sub>2</sub>/N<sub>2</sub> selectivity, increasing from 7.3 to 71.

### 3.2. The key for improving environmental impacts of CO<sub>2</sub> capture with HCPs from flow synthesis

From Fig. 3, it was clear that the CO<sub>2</sub>/N<sub>2</sub> selectivity of HCP adsorbents was not key for reducing the environmental impacts of capturing 40 mg of CO<sub>2</sub> from a hypothetical 85:15 CO<sub>2</sub>/N<sub>2</sub> mixture at 25 °C and 1 atm. This was because amongst all HCPs studied here, the CO<sub>2</sub>/N<sub>2</sub> selectivity of internally crosslinked HCPs synthesised in flow reactions was the highest, reaching a value of 71 (Table 1). Meanwhile, the CO<sub>2</sub>/N<sub>2</sub> selectivities of externally and post-crosslinked HCPs synthesised in flow reactions were 23 % and 25 % lower than those yielded from batch reactions. With lower CO<sub>2</sub>/N<sub>2</sub> selectivities, 41 % and 55 % more post-

crosslinked and external crosslinked HCPs synthesised *via* flow reactions were required to capture 40 mg of CO<sub>2</sub>. In contrast, 36 % less internally crosslinked HCPs were required for the same application. Based on this data, it appeared that product yield of continuous flow reactions was key for lowering impact scores, *i.e.*, improving environmental impact (Fig. 4).

As shown in Fig. 4, the transition to flow synthesis resulted in the most significant adverse changes in environmental impacts for the internal crosslinking strategy, followed by external crosslinking and post-crosslinking. This order followed the trend of addition chemical consumption for each crosslinking approach after implementing flow system. In flow synthesis, the amount of consumed chemicals for internal, external, and post-crosslinking were higher than those in batch syntheses by averagely 5.2-, 2.1-, and 1.7-fold, respectively (Table 3). Meanwhile, a similar trend was also observed in the change in product yield from these three crosslinking strategies when switching from batch to flow synthesis. As batch reactions were replaced with flow synthesis, the product yield from internal, external, and post-crosslinking reduced by 87 %, 27 %, and 18 %, respectively. These trends suggested that the most adverse environmental impact changes that were associated with the internal crosslinking approach when flow reactor was implemented into HCP synthesis process (36 % and 15 % reduction in score for Climate change and Resources endpoint categories, 197 % and 19 % increment in score for Ecosystem quality and Human health endpoint categories) were likely related to the low product yield percentage. The 7 % yield of internal crosslinking could be due to the absence of an additional crosslinker in the system, which caused a slower kinetic rate compared to the other two synthetic approaches [32]. Synthesising HCPs *via* post-, and external crosslinking in flow synthesis approached our aim of delivering a HCP production technology that is more environmentally sustainable than existing batch methods, *i.e.*, reducing environmental impact scores in all four categories. In post-crosslinking,

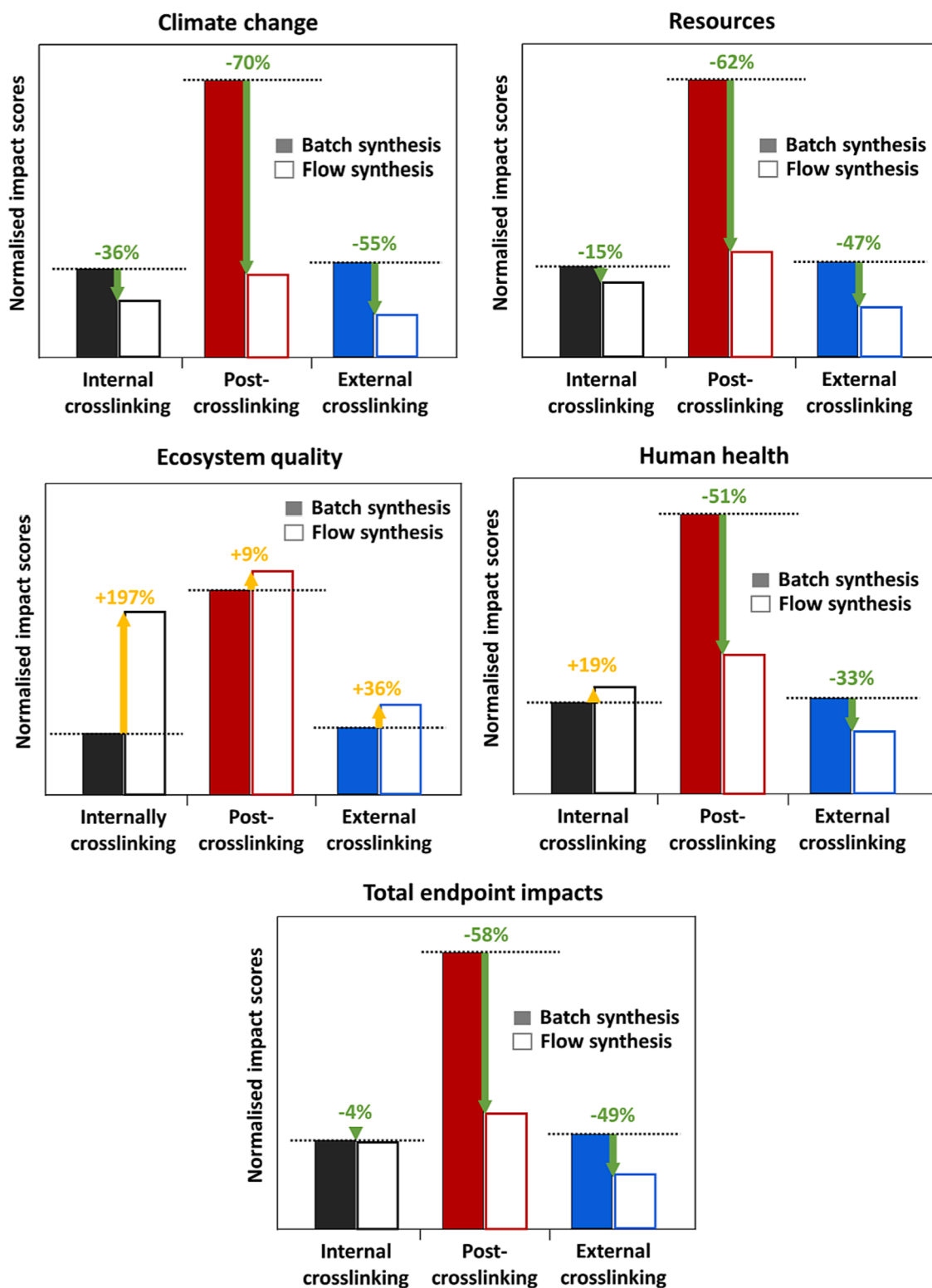


Fig. 3. Normalised endpoint impact scores for each synthesis process of three HCP types for capturing 40 mg CO<sub>2</sub> via low-pressure adsorption. The change in impact scores from batch synthesis to flow synthesis was highlighted with arrows for each synthetic approach.

the scores of 3 out of 4 endpoint impacts – Climate change, Resources, and Human health were reduced. This could be attributed to a 10 fold decrease in electricity consumption (resulting from a 99 % shorter reaction time [20]), despite consuming 1.7-fold more chemicals consumption (Table 3) and 18 % less product yield. This was also the same for external crosslinking in continuous flow reactions where a 4.8-fold

reduction in electricity consumption offset the effects of a product yield that was 27 % lower and consuming 2.1 fold more chemicals.

Among the three HCP crosslinking strategies that were performed in continuous flow reactions in comparison with the batch reactions, internal crosslinking was the system that required the most improvement in the aspect of environmental adverse effects. This was ascribed to

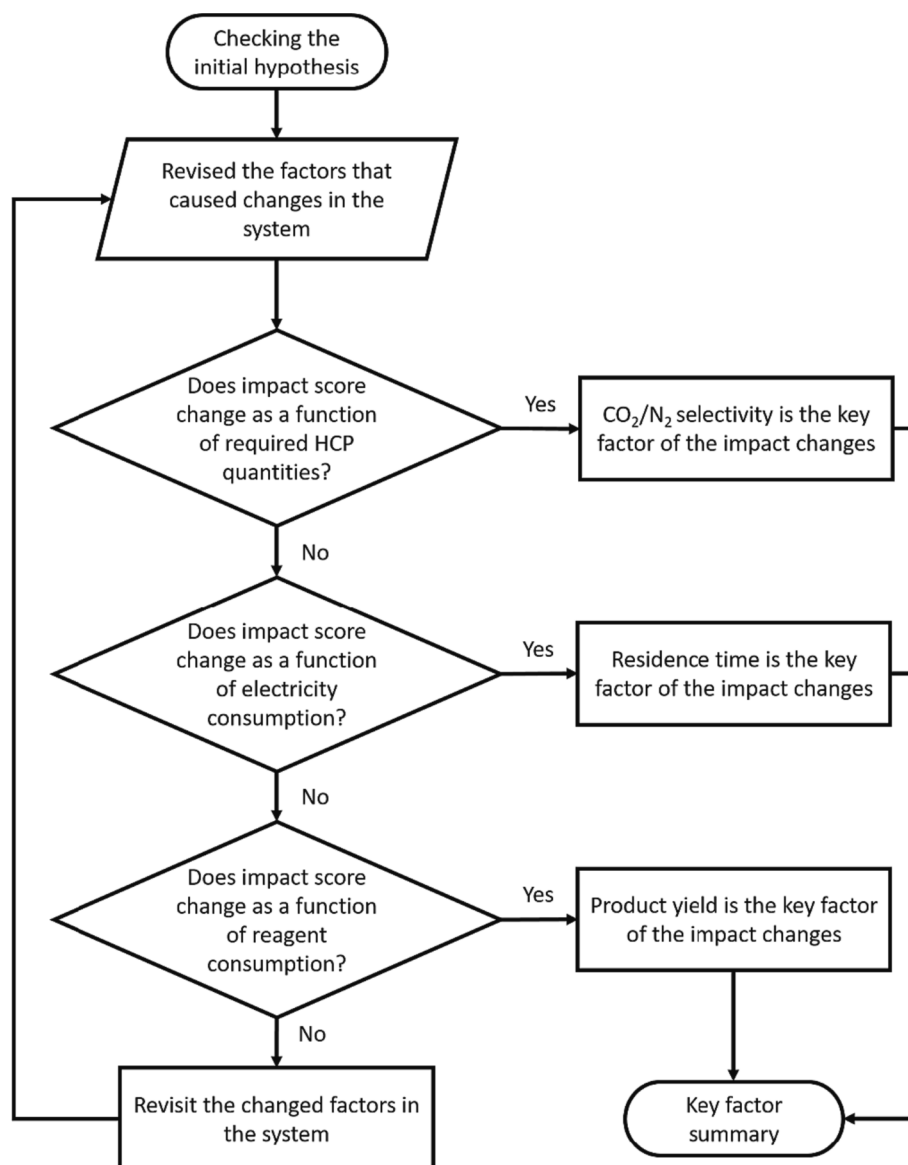


Fig. 4. The flowchart showing the thought process of which factor is the key of changing of impact scores.

increments in Ecosystem quality and Human health impact scores, and the lowest reduction of Climate change and Resources endpoint impact scores (36 % and 15 %, respectively). This was due to the reduction of product yield by 88 %, which reached a level where the impact scores from a 5.2-fold increase in chemical consumption outweighed the lower impact scores associated with a 12-fold reduction in electricity consumption. The product yield could be improved either through modifications to the flow reactor or further optimisation of operating conditions. This could then reduce the scores for the overall endpoint impacts of the internal crosslinking approach *via* flow synthesis. Therefore, identifying the threshold product yield that offsets the impact of higher chemical consumption and lower electricity consumption could potentially achieve lower scores for all four endpoint impacts in HCP flow synthesis.

More details regarding the environmental impacts of HCP synthesis for all three crosslinking strategies, using both batch and flow systems, could be identified from midpoint impacts. The interpretation of midpoint impact is based on the reference substances in their units [33]. For instance, Terrestrial ecotoxicity midpoint impact under the Ecosystem quality endpoint impact represents the equivalent weight in kilogram of triethylene glycol (TEG) emitted into the soil. It indicates

that Terrestrial ecotoxicity midpoint impact represents the amount, in kilogram, of components that have the same effect as TEG that emitted into the soil. However, it is not necessary for TEG to be presented within the system boundary. The midpoint impacts that accounted for the highest impact in each endpoint were identified based on the highest normalised midpoint impact score among all midpoint impacts within the same endpoint category (Figure S1). The only midpoint impact under Climate change endpoint category is Global warming, which represents the amount of emitted CO<sub>2</sub> equivalents in kilogram. Therefore, the decrease in the score for Climate change endpoint impact equalled to the decrease in the Global warming midpoint impact [31]. This indicated that implementing the flow system in HCP synthesis *via* internal, post-, and external crosslinking to produce the required amounts of HCPs for capturing 40 mg of CO<sub>2</sub> could reduce emissions of CO<sub>2</sub> and other greenhouse gases associated with global warming by 36 %, 70 %, and 55 % on a kilogram basis (Figure S2).

The key midpoint impact that contributed to the Resources endpoint category was Non-renewable energy, which accounted for 100 % of the total midpoint impact scores within the Resources endpoint category for all three crosslinking strategies using both batch and flow systems. Non-renewable energy midpoint impact refers to the amount of energy

utilised, measured in MJ, extracted from primary non-renewable resources such as crude oil equivalent [34]. The decrease in the score for Non-renewable energy midpoint impact for internal, post-, and external crosslinking when using flow instead of batch reactions indicated that synthesising the required amount of HCPs with flow synthesis for capturing 40 mg of CO<sub>2</sub> could reduce the energy extracted from crude oil equivalent by 15 %, 62 %, and 47 % on MJ basis, respectively (Figure S3). For Ecosystem quality endpoint category, Terrestrial ecotoxicity was the major contributing midpoint, accounting for an average of 80 % and 93 % of the total normalised midpoint impact scores within the Ecosystem quality endpoint category for batch and flow syntheses, respectively, for all three crosslinking approaches. The increase in scores for Terrestrial ecotoxicity from batch to flow synthesis indicated that the synthesis of the required amount of HCPs for 40 mg CO<sub>2</sub> adsorption using continuous flow reactions would release a higher amount (in kilogram basis) of TEG equivalent into the soil compared to using the batch system by 254 %, 27 %, and 57 % for internal, post-, and external crosslinking, respectively (Figure S4). The highest normalised score percentage of midpoint impact under Human health endpoint category was Respiratory inorganics, which was averaged 91 % and 83 % for batch and flow systems, respectively, across all three crosslinking strategies. Respiratory inorganics midpoint impact represents the emitted PM<sub>2.5</sub> equivalent weight in kilograms into air [31]. The change in scores for Respiratory inorganics when switching from batch to flow synthesis indicated that, in order to produce the required amount of HCPs for capturing 40 mg of CO<sub>2</sub>, flow synthesis of internal crosslinking would result in a 6 % higher of PM<sub>2.5</sub> equivalent weight emitted, while flow synthesis of post- and external crosslinking would reduce the PM<sub>2.5</sub> equivalent weight by 56 % and 39 %, respectively, when compared to batch synthesis (Figure S5). By identifying the major contributing midpoint impact of each endpoint category, we could specifically focus on reducing these major attributed midpoint impacts from flow synthesis of HCPs alongside improving product yield.

### 3.3. Sensitivity analysis

A sensitivity analysis is typically used to identify how a key parameter of a system can affect outcomes in different scenarios. As we pointed out that product yield was the key factor of our system, the purpose of this sensitivity analysis was to determine the minimum product yield of

internal crosslinking using continuous flow synthesis that could overcome increments in impact scores associated with consuming more chemicals. Here we assigned the actual yields from batch and flow synthesis of internal crosslinking as 1.655 g and 1.055 g, respectively. These values corresponded to the amount of HCP adsorbents required for capturing 40 mg of CO<sub>2</sub>. This assessment focused on the scores of the four highest normalised percentage midpoint impacts in each endpoint category, namely, Global warming in Climate change, Non-renewable energy in Resources, Terrestrial ecotoxicity in Ecosystem quality, and Respiratory inorganics in Human health. It should be noted that increasing product yield of continuous flow synthesis would require improvements in heat and mass transfer, leading to suitable mixing and enhanced reaction rates [20]. This could potentially involve a continuous flow reactor with different specifications, for instance, coil diameter, pitch length, and pipe diameter [35].

From Fig. 5, it was clear that even without improving product yield, the Global warming (green) and Non-renewable energy (yellow) midpoint impact scores of internal crosslinking in continuous flow reactions were already lower than those of batch synthesis. If the product yield of this synthesis approach processes was to increase by ~10 %, *i.e.*, reaching to 8 %, the score for Respiratory inorganics would be the same as those from batch reactions. This way the approach of continuous flow synthesis would cause less burden on the endpoint impact of Human health. At this point, the score for Terrestrial ecotoxicity midpoint impact of flow synthesis remained higher than the benchmark score by 228 %, indicating that flow synthesis of internally crosslinked HCPs was not more environmentally sustainable than batch synthesis. For flow synthesis of internally crosslinked HCPs to become more environmentally sustainable than batch synthesis, the product yield of the former process must be improved by 250 %, *i.e.*, reaching a product yield of 25 %. With a product yield of 25 %, the scores for Terrestrial ecotoxicity in both flow and batch synthesis were the same, while the scores for Global warming, Non-renewable energy, and Respiratory inorganics were reduced by 81 %, 76 %, and 70 %, respectively. This indicated that the 25 % product yield threshold for flow synthesis of internally crosslinked HCPs would result in lower midpoint impacts for all four aspects compared to batch synthesis for capturing 40 mg of CO<sub>2</sub>. In the case where the product yields of flow and batch synthesis of internal crosslinking become identical at 59 %, the midpoint impact scores synthesis for Global warming, Non-renewable energy, Terrestrial ecotoxicity, and

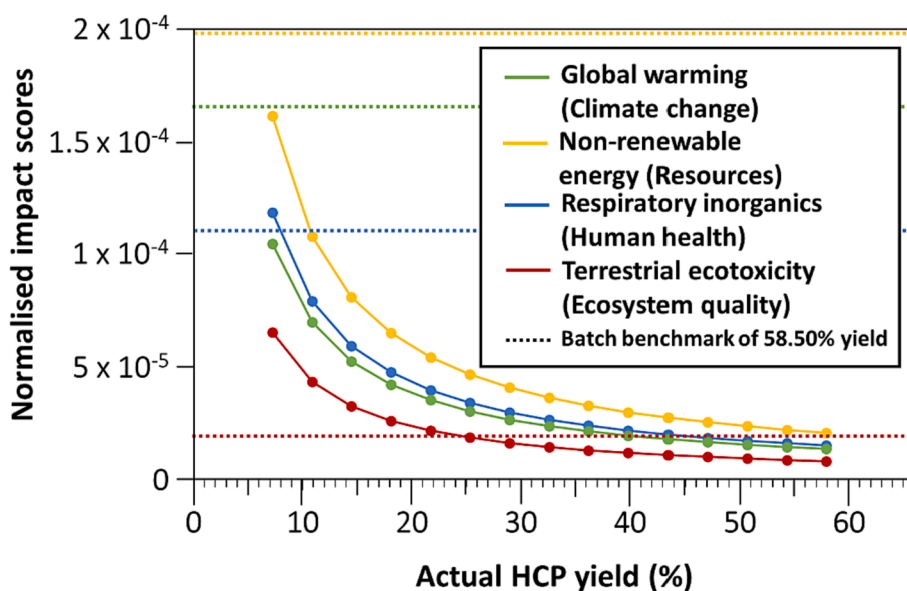


Fig. 5. Normalised impact scores of the synthesis process of p-DCX in flow system at different percent yields of flow-synthesised p-DCX. The solid lines represented the normalised impact scores of flow synthesis of internal crosslinking, while the dotted lines represented the impact scores of the batch synthesis of the same crosslinking approach which had the product yield of 59 %.



Respiratory inorganics would be reduced by 92 %, 89 %, 56 %, and 86 %, respectively. This showed that it was unnecessary to develop a flow reactor to achieve 59 % product yield for flow synthesis of internally crosslinked HCPs as lower environmental impacts could also be delivered with a yield of 25 %.

#### 4. Conclusion

Herein, the environmental assessment of HCP synthesis for carbon capture was conducted using the LCA method. The study aimed to compare the environmental sustainability of the traditional batch with the innovative approach of flow synthesis. Results showed that continuous flow reactions was capable of reducing the environmental impact of synthesising HCPs for carbon capture, but could be further improved. Amongst the different crosslinking strategies studied here in this work, LCA findings indicated that continuous flow synthesis offered the most reduction in environmental impacts when post-crosslinking was performed, followed by external crosslinking, and lastly internal crosslinking. This finding contradicted our initial hypothesis that high CO<sub>2</sub>/N<sub>2</sub> selectivity in HCPs synthesised in flow synthesis would reduce environmental impacts by reducing the mass of HCPs required for capturing 40 mg of CO<sub>2</sub>. Instead, our work here showed that key for achieving an environmentally sustainable HCP synthesis method was product yield. This was validated with a sensitivity analysis where we showed that if product yield of flow synthesis improved from the current value of 7 % to 25 %, all the scores for key midpoint and endpoint impacts would be lower than those from batch reactions. Hence, we recommended that future research should prioritise achieving this minimum threshold of product yield over developing new materials with exemplary CO<sub>2</sub>/N<sub>2</sub> selectivity. With advantages such as environmental impact reduction, high CO<sub>2</sub> capture performance, and high productivity, continuous flow synthesis should be widely deployed to scale up HCP production in industry.

Suggestions for future investigations, two major key factor should be considered. The CO<sub>2</sub>/H<sub>2</sub>O selectivity of HCPs warrants attention, especially considering that that flue gas often comprises a similar weight percentage of H<sub>2</sub>O steam as CO<sub>2</sub> [36,37], potentially leading to competition for adsorption sites. Competitive sorption between CO<sub>2</sub> and water has been observed in conditions, leading to lower CO<sub>2</sub> adsorption capacities in HCPs similar to the ones studies here [38]. Consequently, this could require a higher amount of HCPs for effective CO<sub>2</sub> adsorption. Conversely, the regeneration stage of HCPs should also be addressed. This is equally crucial to trade-off with the aforementioned concern. Previous investigations show that HCPs can be recycled for multiple adsorption cycles [7,39], with one of the study indicating only a 2 % decrease in CO<sub>2</sub> adsorption after ten cycles [40]. This potential for recycling could substantially reduce the required amount of HCPs for CO<sub>2</sub> capture. However, evaluating the effect of regeneration will require an extension of the system boundary to encompass the utilisation stage, specifically covering the electricity consumption during desorption. Taking these two key factors into account would not only add practicality to the outcomes but may enhance the credibility of continuous flow system for implement in industrial manufacturing.

#### Author contributions

The research was proposed by C. H. L. The conceptualised framework was discussed between N. C. and C. H. L. The laboratory experiment, CO<sub>2</sub> adsorption and CO<sub>2</sub>/N<sub>2</sub> selectivity data was retrieved from our previous work. The paper was written, revised and edited by N. C. and C. H. L.

#### CRedit authorship contribution statement

**Nadhita Chanchaona:** Conceptualization, Methodology, Software, Formal analysis, Writing – original draft, Writing – review & editing,

Visualization, Funding acquisition. **Cher Hon Lau:** Conceptualization, Writing – review & editing, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.125145>.

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