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Continuous flow synthesis of hypercrosslinked polymers (HCPs) and its environmental impact evaluation

Nadhita Chanchaona



THE UNIVERSITY
of EDINBURGH

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School of Engineering

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Thesis declaration

I declare that this thesis has been composed solely by myself and that it has not been submitted in any previous application for any degree or professional qualification. I confirm that the work submitted is my own, except where work which has formed part of jointly-authored publications has been included. My contribution and those of the other authors to this work have been explicitly indicated below. I confirm that appropriate credit has been given within this thesis where reference has been made to the work of others.

The work presented in Chapter 3 was previously published in Journal of Material A as 'Flow synthesis of hypercrosslinked polymers with additional microporosity that enhance CO₂/N₂ separations' by **Nadhita Chanchaona**, Liang Ding, Shiliang Lin, Sulaiman Sarwar, Simone Dimartino, Ashleigh J. Fletcher, Daniel M. Dawson, Kristina Konstas, Matthew R. Hill, **Cher Hon Lau**. This study was conceived by all of the authors. I carried out methodology, investigation, formal analysis, visualisation, and writing – original draft, review & editing.

The work presented in Chapter 4 was previously published in Industrial & Engineering Chemistry Research as 'Analyzing environmental impacts of hypercrosslinked polymers produced from continuous flow synthesis for water treatment' by **Nadhita Chanchaona** and **Cher Hon Lau**. This study was conceived by all of the authors. I proposed and conceptualised the research idea and carried out methodology, investigation, software, formal analysis, visualisation, and writing – original draft, review & editing.

The work presented in Chapter 5 was previously published in Separation and Purification Technology as 'Assessing the environmental impact of hypercrosslinked polymers for low-pressure CO₂ adsorption' by **Nadhita Chanchaona** and **Cher Hon Lau**. This study was conceived by all of the authors. I proposed and conceptualised the research idea and carried out methodology, software, formal analysis, visualisation, and writing – original draft, review & editing.

The data presented in the first half of the work presented in Chapter 6 was obtained in an experiment carried out by Nikita Rog and Karisma Kapur in the University of Edinburgh. I was the co-supervisor of these research projects and co-contributed to these roles: conceptualisation, methodology, investigation, and formal analysis.

The data presented in the second half of the work presented in Chapter 6 was obtained in an experiment carried out by me in Queen's University Belfast with the assistance of Stuart L. James, Beibei Li, and Niamh Curran. I proposed and conceptualised the research idea and carried out methodology, investigation, and formal analysis.

Nadhita Chanchaona

Abstract

Hypercrosslinked polymers (HCPs) are a class of microporous adsorbents with a wide range of applications, including dye adsorption, and gas storage. Traditionally, HCPs are synthesised through Friedel-Crafts alkylation, which involves a time-consuming synthesis process in batch reactors, posing challenges for scaling up production to meet global demand. The prolong reaction duration issue could be eliminated by means of a new synthetic method to substitute batch reactors.

The ultimate aim of this study is to intensify the HCP synthesis process by transitioning from batch reactors to continuous reactors. This shift intends to enhance productivity while maintaining a high specific surface area, crucial for superior adsorption capacity. Additionally, this study aspired to reduce the environmental impact associated with this new method for HCP synthesis.

To achieve these objectives, a continuous flow system had been adopted as a replacement for the conventional batch method in HCP synthesis. Three types of HCPs were successfully synthesised using well-established strategies (internally crosslinked, post-crosslinked, and externally crosslinked) in the continuous flow system, showcasing its versatility. The productivity, measured as space-time-yield (STY), of continuous flow synthesis showed an enhancement ranging from 32 – 117-fold when compared to batch synthesis. These improvements were attributed to reducing reaction duration during flow synthesis, from 1440 minutes (24 hours) to 5 – 15 minutes. The specific surface areas of flow-synthesised HCPs were, on average, lower than the batch-synthesised HCPs by 1.5 – 10 %. This meant that when compared to batch-synthesised HCPs, more quantities of flow-synthesised HCPs were needed for dye adsorption and CO₂ capture. However, despite this requirement for larger quantities, the environmental assessment of continuous flow synthesis indicated a reduction in negative environmental impacts across most environmental impact indicators. This suggest an improvement in the environmental sustainability of continuous flow HCP synthesis compared to batch synthesis. Furthermore, this study also explored an alternative synthesis method using twin screw extraction (TSE) with deep eutectic solvents (DES), a benign solvent replacement for halogenated solvents, during HCP synthesis. Although this approach offers promising potential as the replacement of continuous flow synthesis using conventional halogenated solvents, further investigations are warranted for its optimisation.

In conclusion, this thesis advocates for the adoption of continuous flow synthesis of HCPs, underlining its potential for productivity enhancement and reduced environmental impacts. This study lays the foundation for the potential industrial-scale implementation of continuous flow synthesis, bridging the gap between HCP supply and demand while contributing to lower environmental impacts in the production process.

Lay summary

Amongst commercial adsorbents for water treatment, hypercrosslinked polymers (HCPs) has been used for decades after its invention in 1970s. The process to create HCPs is relatively straightforward, involving the mixing and heating of a solution consisting of building blocks, a catalyst, and crosslinker reagents, in a batch tank. However, this process is time-consuming, taking several hours to a 24 hours to complete. In industries, where time is money, speeding up this reaction could become a huge advantage as more product can be potentially produced in the same amount of operating time, leading to meeting supply demands for a growing market and higher profitability.

In this study, this limitation was resolved by replacing the traditional batch reactor with a continuous flow reactor for the HCP synthesis process. The design of continuous flow reactor is similar to a tube reactor, featuring a greater surface area along its wall, while occupying less volume compared to the batch tank. These characteristics of continuous flow improved heat and mass transfer rates, analogous to the concept of cooking. Imagine cooking a same amount of minced chicken against a whole chicken breast fillet with a cooking pan at the same temperature for the same duration. Minced chicken would cook faster because heat can readily pass through its larger contact area. Also, minced chicken can be easily stirred, altering the contact area with the cooking pan. Similarly, continuous flow reactor promotes more efficient reactions, resulting in higher productivity, which refers to the amount of products per stipulated operating time per volume of reactor.

By using a continuous flow system to produce three HCP types, this method was proven capable to reduce reaction duration from 24 hours to 5 – 15 minutes. This reduction in reaction duration led to productivity increases of 32 – 117 times when compared to the batch synthesis process. It was also essential to verify the specific surface area of HCPs, a characteristic indicative of their general performance as adsorbents. HCPs synthesised from the continuous flow method exhibited a lower specific surface area, 1.5 – 10 % less compared to those produced using batch synthesis. Consequently, when compared to those of batch synthesis, more HCPs synthesised from continuous flow were required for applications in removing dyes from water and separating carbon dioxide from nitrogen. Despite requiring more flow-synthesised HCPs during applications, the continuous flow synthesis method demonstrated environmental benefits by reducing negative impacts across most aspects, particularly in terms of carbon dioxide emission, resource depletion, and effect on human health. Moreover, an alternative synthesis method, known as twin screw extrusion (TSE) was explored as a potential choice for continuous synthesis of HCPs using a less hazardous solvent. However, this work needs further investigation involving the adjustment of operating factors to achieve the promising quality of HCPs.

In summary, the adoption of a continuous flow system enhanced the productivity of HCP synthesis process. The potential impact of this work is substantial, particularly when implemented at a larger manufacturing scale. As this research indicates, the advantages of the continuous flow system extend beyond economic benefit; they also contribute positively to environmental sustainability.

Publications and conferences

First-author publications:

1. **Chanchaona, N.**; Ding, L.; Lin, S.; Sarwar, S.; Dimartino S.; Fletcher, A. J.; Dawson, D. M.; Konstas, K.; Hill, M. R.; Lau, C. H., Flow synthesis of hypercrosslinked polymers with additional microporosity that enhance CO₂/N₂ separations. *Journal of Material A* 2023, 11 (1), 9859-9867. <https://doi.org/10.1039/D2TA09253K>.
2. **Chanchaona, N.**; Lau, C. H., Analyzing environmental impacts of hypercrosslinked polymers produced from continuous flow synthesis for water treatment. *Industrial & Engineering Chemistry Research* 2023, 62 (23), 9046-9053. <https://doi.org/10.1021/acs.iecr.3c00829>.
3. **Chanchaona, N.**; Lau, C. H., Assessing the environmental impact of hypercrosslinked polymers for low-pressure CO₂ adsorption. *Separation and Purification Technology* 2023, 329 (1), 125145. <https://doi.org/10.1016/j.seppur.2023.125145>.

Co-author publications (Under reviewing):

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Corresponding author publications:

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Conferences:

1. **Chanchaona, N.**; Lau, C. H.; Gerogiorgis, D., Generalisation of hypercrosslinked polymer synthesis *via* continuous flow system (Poster). University of Edinburgh School of Engineering PGR Conference (Online) 2021, Edinburgh (UK).
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2. Rog, N.; **Chanchaona, N.**; Lau, C. H., Development of a Flow Reactor for Sustainable Production of Polymers. CHEE11017 Chemical Engineering Design Research Project 5, 2021-2022.
3. Kapur, K.; **Chanchaona, N.**; Lau, C. H., Scale up manufacturing of microporous polymers. CHEE11017 Chemical Engineering Design Research Project 5, 2022-2023.

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Abbreviations

BET:	Brunauer-Emmett-Teller
ChCl:	Choline chloride
DCE:	1,2-dichloroethane
DCX:	α , α' -dichloro- <i>p</i> -xylene
DES:	Deep eutectic solvent
FDA:	Formaldehyde dimethyl acetal
FeCl ₃ :	Iron (III) chloride
HCP:	Hypercrosslinked polymer
LCA:	Life-cycle analysis
PS:	Polystyrene
RB:	Rhodamine B
TSE:	Twin screw extrusion
UA:	Uniblue A
ZnCl ₂ :	Zinc (II) chloride

1. Introduction

1.1. Hypercrosslinked polymers

Hypercrosslinked polymers (HCPs) are a distinct class of polymers characterised by a dense network of crosslinks within an amorphous structure, distinguishing them from conventional crosslinked polymers such as polystyrene (PS) or poly(styrene-co-divinylbenzene) (PS-DVB).¹ The hypercrosslinking process results in HCPs having a high density of both mesopores and micropores.² This, in turn, leads to exceptional specific surface areas and performance in applications comparable to other porous materials, for example, zeolites, activated carbons, and metal organic frameworks.³ HCPs belong to the category of porous organic polymers, alongside polymers of intrinsic microporosity,² covalent organic frameworks, conjugated microporous polymers, covalent triazine frameworks, and porous aromatic frameworks.¹

Introduced in the 1970s by Tsyurupa and Davankov,⁴ HCPs were invented to overcome the limited crosslinking degree in macroporous PS-DVBs synthesised *via* conventional suspension polymerisation. Due to steric congestion and phase separations, a significant amount of vinyl groups is unable to form an extensive crosslinked structure. A typical method to hypercrosslink these slightly crosslinked polymers consists of three steps.⁵ First, the precursor is soaked and swollen in a solvent to untangle the polymeric chains. The resulting free space occupied by the solvent allows for the formation of numerous crosslinked bridges, leading to an extensive immobilised amorphous network. These linkages formed through Friedel-Crafts alkylation with the addition of crosslinking agents. Finally, the solvent is removed, unveiling rigid hypercrosslinked frameworks. As a result of the secondary hypercrosslinking process, HCPs comprise micropores and mesopores as opposed to the macroporous structure of their original precursor. The product of this approach is known as Davankov's resin, named after its inventor.² Several companies have commercialised this type of HCP as ion-exchange resins under various brands, including Purolite's Macronet™, DowDupont Inc.'s Amberlite™, and Lanxess AG's Lewatit® series.⁶

Following the breakthrough of Davankov's resin, researchers further adapted the synthesis method by modifying substrates or crosslinkers, resulting in the emergence of new varieties of HCPs. Tan and Tan² categorised these HCP species based on their synthetic approaches. The original approach introduced by Davankov is referred as post-crosslinking. The second approach is known as internal crosslinking. This method was developed for one-pot synthesis, eliminating the need for the former suspension polymerisation step. The mechanism of this approach is akin to condensation polymerisation and requires the use of bifunctional monomer reagents, which were previously employed as external crosslinkers in the post-crosslinker approach. Examples of such bifunctional monomers¹ include α,α' -dichloro-*p*-xylene (DCX), 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP), and 9,10-bis(chloromethyl)anthracene (BCMA). The most recent synthetic approach, reported in 2011, is known as external crosslinking or the knitting strategy.⁷ The introduction of formaldehyde dimethyl acetal (FDA) as an external crosslinker has overcome the limitation of building block

choices, allowing for the use of a wide range of aromatic compounds. With this approach, the HCP library has expanded significantly over the past decade, encompassing structures ranging from the simple benzene ring⁷ to complex 3D structures like triptycene,⁸ and even incorporating heterocyclic compounds.⁹

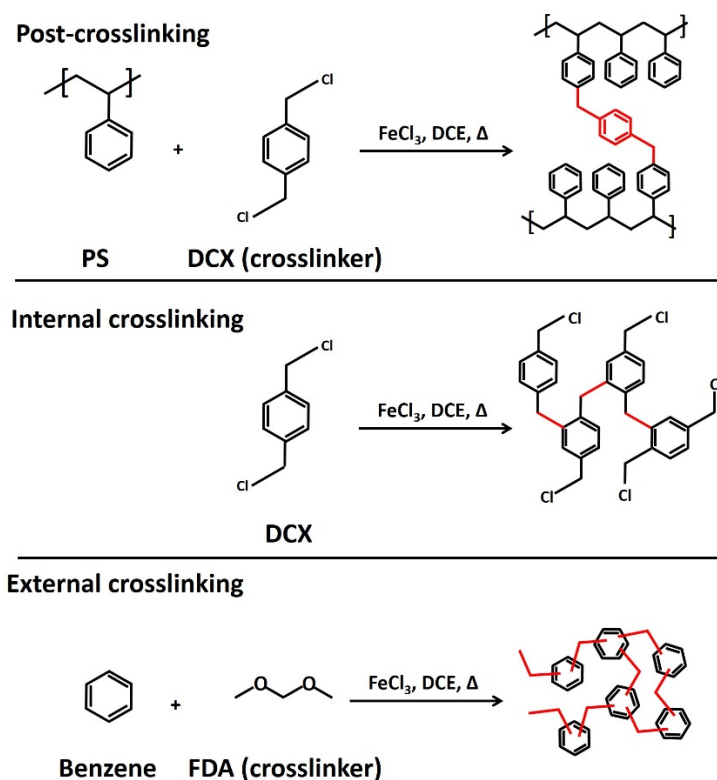


Figure 1 Example of three synthetic approaches of HCPs

Regardless of the chosen synthetic approach, Friedel-Crafts alkylation (Figure 2) is exploited to form crosslink bridges. This reaction necessitates two essential reagents – a catalyst and a solvent, aside from the precursor and crosslinker. The typical catalyst used for Friedel-Crafts alkylation is a Lewis acid. Amongst Lewis acids, iron (III) chloride (FeCl_3) is widely favoured for its high reactivity, resulting in HCPs with a superior specific surface area.³ Other Lewis acids such as aluminium (III) chloride (AlCl_3),^{10–12} tin (IV) chloride (SnCl_4),¹³ zinc (II) chloride (ZnCl_2),¹⁴ are predicted to have either poor solubility or steric hindrance, making them unsuitable for HCP synthesis.³ The choice of solvent used in the hypercrosslinking process depends on its ability to dissolve or swell the selected precursors.³ This suitable solvent, known as a thermodynamically good solvent, can be determined using Hildebrand and Hansen solubility parameters.¹⁵ The preferred choice of the thermodynamically good solvent for HCP synthesis in several literatures is 1,2-dichloroethane (DCE).³ DCE can also act as a crosslinker in the system, as evidenced by the formation of $-\text{CH}_2\text{CH}_2-$ crosslinking bridges on waste-expanded polystyrene precursor in the absence of an external crosslinker.¹⁶ Another crucial condition to activate and/or accelerate the crosslink bridge formation *via* Friedel-Crafts alkylation is heat.¹⁷ The common temperature for the synthesis of hypercrosslinked polymers using FeCl_3 and DCE as catalyst and solvent, respectively, is set to 80 °C. At this temperature, the formation of crosslink bridges at the expected level, based on

the general range of BET surface area of common HCPs, could be obtained within a day. There was a report of using room temperature to synthesise p-DCX, the product with the BET surface area of $1400 \text{ m}^2 \text{ g}^{-1}$ was able to obtain within a week long instead.¹⁸

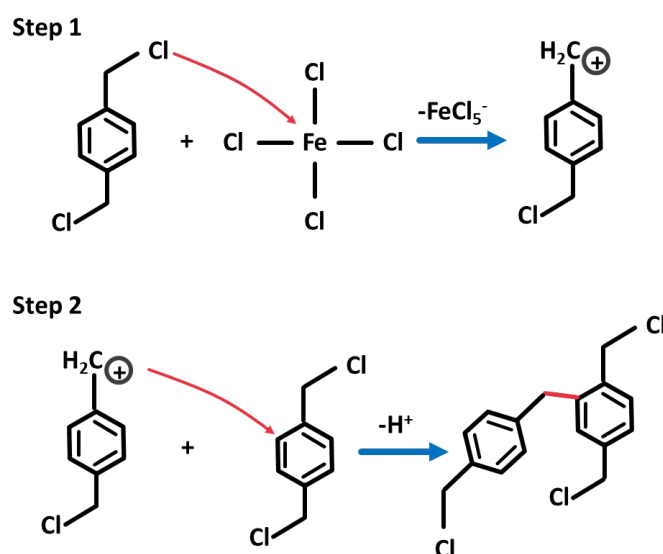


Figure 2 Mechanism of crosslink bridge formation via Friedel-Crafts alkylation using p-DCX as example

Over the years, various combinations of reagents have been employed to synthesise HCPs, resulting in a diverse range of materials. Numerous HCPs have been reported to possess Brunauer-Emmett-Teller (BET) surface areas ranging from 400 to $2400 \text{ m}^2 \text{ g}^{-1}$.¹⁻³ This impressive specific surface area is typically associated with the intensive degree of crosslinking within the structure.² A higher specific surface area usually translates to more adsorption site within HCPs, leading to enhanced adsorption capacity.¹⁹ Therefore, the determination of specific surface area, along with other textural properties like pore size distribution, serves as a key characteristic underpinning their potential for real-world applications. Commercialised ion exchange resins, *i.e.*, post-crosslinked HCPs are well-known for their use in industrial wastewater treatment. They have been effectively employed for the removal of pesticide,²⁰ polyaromatic hydrocarbons,²¹ and separation of mineral ions.²² For instance, in the presence of natural organic matter, ion exchange resins exhibited a 10 % reduction in capacity compared to pure pesticide adsorption, whereas activated carbons showed an 80 % reduction in capacity. Although the final adsorption capacities were the same between ion exchange resins and activated carbons, due to the significantly adsorption capacity of activated carbons in pure pesticide, it indicated that ion exchange resins would have a longer operating life than activated carbons in practical applications.²⁰ The global market for ion exchange resins has been steadily growing with estimated demands of US\$ 1.8 billion in 2020 and projected demands of US\$ 2.2 billion in 2025.²³ In laboratory-scale studies, HCPs synthesised through internal and external crosslinking approaches have demonstrated excellent adsorption properties across various applications, including gas storage,^{7, 8, 12, 24-33} gas separation,^{9, 16, 18, 34-40} volatile compound removal,⁴¹⁻⁴⁴ warfare agent adsorption,⁴⁵ downstream separation in biorefinery process,⁴⁶ catalysts,^{47, 48} supercapacitors,⁴⁹ and wastewater treatment subcategories.^{8, 11, 14, 34, 49-55} As HCPs have demonstrated their versatility and high performance across various applications, it is essential to explore

innovative synthesis methods that can enhance productivity in their production. The global demands for HCPs could potentially exceed current projections as they find new applications beyond water treatment. Therefore, innovative methods are necessary to keep pace with the growing demand for HCPs.

1.2. Flow chemistry

In the context of synthesising commercialised HCPs, it is noteworthy that large-scale production predominantly adheres to the conventional batch synthesis methodology.⁵⁶ This traditional method entails prolonged mixing and heating processes to attain the desired level of crosslinked network within the HCP structure. Especially when applied at manufacturing scale, this procedure can become considerably time-intensive due to inherent challenges associated with heat and mass transfer in larger tank volumes, often used to operate for several tonnes per day. Consequently, it frequently yields non-uniform blending and inconsistent product quality.⁵⁷ To mitigate these existing issues, efforts have been made to improve tank design, including agitators and baffles. However, the increasing demand for HCPs presents its own set of challenge, which, in turn, necessitates additional land area and infrastructure investments for more batch reactors. Alternatively, an innovative approach involving the modification of conventional reactor structure,⁵⁸ could provide solutions to all these challenges.

Flow chemistry offers a prominent alternative for the synthesis of porous materials.⁵⁹ The principle of flow synthesis is akin to a series of continuous-stirred tank reactor (CSTR). Each section of the flow reactor represents a small tank, and the reaction progresses as the fluid travels forward to the next section, similar to transferring to another tank in a CSTR-in-series configuration.⁶⁰ The fundamental components of a flow system include reagent deliverers, tubing, mixers, and reactors (Figure 3).⁶¹ This complex flow system can be customised to align with research requirements, allowing for the incorporation of optional heat sources, quench controllers, pressure regulators, analysers, and more.⁶² Typically, a pump is employed to deliver reagents into the system, and various types of pumps are available to suit the purpose of the flow system. For example, peristaltic pumps are suitable for driving high flow rates, syringe pumps offer high flow stability, and high-performance liquid chromatography pump provide excellent overall control, albeit a higher cost.⁶³ In chemical processes, fluoropolymer-based tubing, especially polytetrafluoroethylene (PTFE), is highly resilient and can withstand harsh operating conditions up to 250 °C and 100 bar. Fluorinated ethylene propylene can be a more affordable choice of tubing material with moderate robustness.⁶¹ It is important to ensure that the plastic material used for the tubing is compatible with other flow accessories like ferrule, nut, and mixer. Mixers serve to connect multiple feed streams, and two common mixer shapes are T- and Y-junctions. Each influencing fluid control and mixing performance based on their different entrance angles.^{64, 65} The flow reactor, where the reaction occurs, is generally a tubular passage. Similar to mixers, the design of the reactor can affect the flow profile, which in turn influences the reaction rate. Reactors can be a single straight tube known as plug flow reactor (PFR),^{57, 66} a coil reactor,^{67, 68} an on-chip design,⁶⁹ or a more complex configuration.^{69, 70}

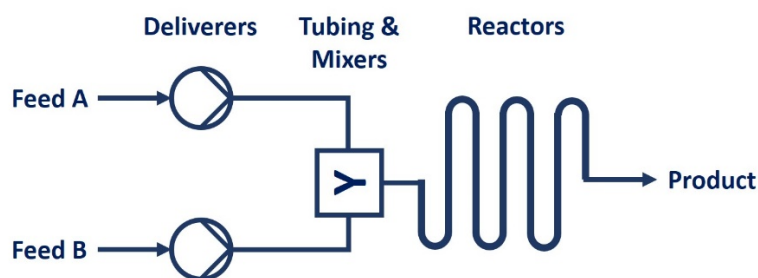


Figure 3 Simplified schematic of continuous flow system for general synthesis reaction

As continuous flow implies process intensification,⁷¹ several benefits arise from transitioning away from the traditional batch system.^{69, 72} One of the key advantages of flow synthesis is increased productivity. The design of a flow reactor also contributes to higher productivity and efficiency. Flow synthesis typically employs a tubular reactor design.^{64, 73} Tube reactors have a small volume with a large surface area, *i.e.*, high specific surface area compared to batch reactors. This high surface area-to-volume ratio offers passive mixing, intensifies heat and mass transfer rates, and accelerates reaction rates.⁷³ For instance, when synthesising covalent organic frameworks and metal organic frameworks using a continuous flow reactor, the reaction time improved significantly compared to batch synthesis. The reaction time decreased from 3 days in the batch reactor to 11 seconds and 15 minutes, respectively. This led to a remarkable increase in space-time-yield (STY), a measurement term of productivity, by 30-fold and 90-fold, respectively.^{66, 74} Additionally, the small characteristic dimension of flow reactors also limits chemical handling to a small volume, enhancing quality controls and safety levels, particularly for highly concentrated mixtures and thermal runaway reactions.⁷² For instance, in the production of ethylene oxide, involves the use of ethylene and oxygen as the main reagents, it is desirable to use pure oxygen as an oxidiser rather than ambient air containing nitrogen, as pure oxygen allows for higher reaction rates.⁷⁵ However, a high oxygen level in the system can increase the risk of explosions.⁷⁶ In a study using a microreactor operating in a continuous manner, it was found that this approach reduced the explosion risk compared to a conventional continuous-stirred tank reactor, allowing for a higher molar percentage of oxygen in the feed mixture, increasing it from 12 % to 53 %.^{76, 77} With a continuous process, the transition stages involved in production, such as transferring the final product from one batch and preparing reagents for the next batch, can be eliminated. This leads to improved production rates. Simultaneously, manual workload is reduced, resulting in lower labour costs.^{78, 79} For instance, an economic analysis of a 2000 L monoclonal antibody production reported a reduction in manual labour costs from 9 % of the overall cost of goods when using 12 units of 500 L batch bioreactors to an average of 5.5 % when using continuous bioreactors.⁸⁰ Moreover, real-time quality inspection can be implemented in the flow system since the tubular design of the reactor allows for observing the progression of the reaction along the streamline.⁸¹ All these advantages can be achieved with just a single tube reactor. Scalability can be accomplished by bundling several identical tube reactors. This is in contrast to scaling up HCP production using batch reactors, which requires multiple large tanks, consuming a significant amount of land area and necessitating substantial infrastructure investments.⁸² Considering these benefits, it is worthwhile to implement continuous flow synthesis of HCPs on a laboratory scale as a fundamental protocol.

1.3. Process sustainability: Environmental aspect evaluation

When establishing any process or service, especially at the industrial level, it is crucial to consider not only economic aspect but also environmental aspect. In many commercial endeavours, the primary focus tends to be on maximising profits, sometimes at the expense of other critical considerations. However, since the 1990s,⁸³ there has been a growing awareness of the need to address these broader aspects due to the increasing evidence of a precarious future marked by unpredictable natural disaster and diseases. The importance of promoting sustainability in processes or services has garnered recognition worldwide, with individuals, corporations, and governments all embracing the concept. Explicit measures have developed to standardise the assessment of sustainability in various domains.

In the field of environmental sustainability, a standard scientific-based tool for quantitative evaluation is Life-cycle assessment (LCA).⁸⁴ This relatively young methodology rapidly developed around the 1990s. LCA commonly involves studying an entire process or service, monitoring its impacts and influences throughout its lifecycle. The LCA framework, as defined by ISO 14040 and 14044 standards (Figure 4), comprises four phases: 1) Goal definition, 2) Scope definition, 3) Inventory analysis, and 4) Impact assessment. The interpretation stage, depicted in the figure, is essential throughout these phases, offering valuable feedbacks to ensure meaningful outcomes.⁸⁵

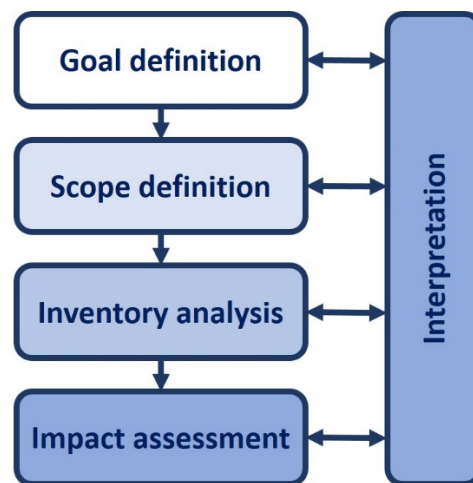


Figure 4 ISO 14040 and 14044 standards LCA framework

To illustrate certain phases of the LCA framework conceptually, one can consider an environmental assessment comparing two rooms with different lighting types as an example. The first phase of the LCA framework is to define the goal of this work. This involves framing the purpose of the assessment, including the questions it intends to answer and the type of answers expected. For instance, in a lighting comparison, the goal might be to determine which type, incandescent bulb vs. fluorescent tubes, has lower environmental impacts. The intended application of the LCA outcomes should be the primary consideration, *for e.g.*, comparing the environmental impacts of multiple processes or services, identifying hotspots of the studied subjects, or developing criteria or policies. It is important to acknowledge the limitations resulting from methodological choices. For instance, comparing the production of a unit of incandescent light bulbs with a unit of fluorescent tubes cannot indicate the

environmental friendliness of the lighting system for a same room, as it excludes other relevant parameters in subsequent stages, such as energy consumption and luminous flux of each lighting type. Considering the target audience also helps guide how the LCA result should be presented and to whom they are relevant.⁸⁵ Overall, this phase greatly influences the conduct of the LCA, as it establishes the framework and narrows down the scope of the assessment.

In the second phase, the details of the LCA are defined. This starts with the establishment of the core reference of the assessment, known as the functional unit. This involves a combination of qualitative and quantitative descriptions to address questions like the subject of analysis, its quantity, the duration of the study, location, and performance parameters. For example, in a lighting comparison, the functional unit might specify a luminous flux of 1000 lux covering an area of 10 m², with a ceiling height of 3 m, assuming 20,000 hours of operation in a room located in the UK. Following the definition of the functional unit, the reference flows are identified, providing quantitative statements related to the functional unit. For the lighting example, these reference flows could consist of 40 units of 100 W A19 incandescent bulb (utilising 2 bulbs at a time with 50 cm spacing between them) and one unit of a 58 W, 1-inch diameter, 1.2 m of fluorescent tube. Another critical aspect of this phase is determining the system boundary. Ideally, an LCA study should encompass the entire life cycle of the process or service, termed cradle-to-grave. However, some studies may focus solely on the production stage up to utilisation, known as cradle-to-gate, or even narrower gate-to-gate processes.⁸⁶ These less common system boundaries have limitations as they may miss potential environmental impacts occurring outside the defined boundary, as mentioned earlier. The system boundary is depicted akin to material and energy balance diagrams, illustrating the included unit processes and flows. Unit processes can be classified into two types: foreground and background processes. Foreground processes rely on primary data specific to the system, while background processes are not system-specific and can be represented with average industry data. In the lighting example, the lighting experiment in the room would be considered a foreground process, while the production of the lighting and electricity generation would be categorised as background processes. Flows within the system boundary are divided into elementary flows and product flows. Elementary flows represent the pathways of resources and emissions and are defined by the International Reference of Life Cycle Data System (ILCD) as substances or energy drawn from the ecosphere, which is the defined boundary without prior human transformation. On the other hand, product flows represent the pathways of the products from one unit process to another within the technosphere, the boundary involving human transformation.⁸⁵ Once all these details, including the system boundary, unit processes, and flows are defined, the inventory analysis is conducted.

The inventory analysis primarily involves data collection. Data accuracy and reliability are reported to allow the audience to trace back all the numerical values to their original data sources. Data quality is classified into five levels, ranging from very low to very high specificity.⁸⁵ Each level has their own specific criteria as following: 1) Data with very low specificity is typically based on the practitioner's judgement. 2) Data with low specificity is obtained from life-cycle inventory databases of relevant processes. 3) Data with medium

specificity is obtained from databases of identical processes. Several process-based life-cycle inventory databases are available, both free and for a fee. These databases include upstream supply chain processes, often used for background processes. Various databases providers offer different types of processes. For instance, the ecoinvent database contains more than 12,500 processes across numerous themes such as transport, energy, materials, and agriculture.⁸⁷ GaBi databases include over 10,000 life-cycle inventory profiles covering topic such as electronics, automobiles, and textiles.⁸⁸ LCA Food provides 600 process data related to fishery, agriculture, and wholesale and supermarket.⁸⁹ 4) Data with high specificity is typically collected through computational modelling. 5) Data with very high specificity is gathered at the direct process site. Reporting data sources is another important factor, and is categorised into three major groups: experts internal to the commissioner (*for e.g.*, process engineers, purchasing departments, researches and development sectors), experts external to the commissioner (*for e.g.*, academic researchers, consultants, industry representatives), and the public (*for e.g.*, other LCA studies, legal documents, consumer organisations). It is also necessary to report the method of data access, indicating whether it was gathered through survey, questionnaire, or directly read-off from on-site scales. Following data collection, the construction of LCA models is carried out using LCA software such as SimaPro,⁸⁸ GaBi,⁸⁸ or OpenLCA.⁹⁰ With the aid of these software and life-cycle inventory assessment methods, the impact assessment of the studied system is conducted.

The impact assessment phase relies on life-cycle inventory assessment methods, which consist of collections of individual characterisation models. Various assessment methods, *for e.g.*, IMPACT World+,⁹¹ ReCiPe,⁹² ILCD,⁹³ have been developed by different companies and are continually updated. Each method features its own calculation formulae, nonetheless, there are similarities in the impact indicators across these methods. Environmental impact indicators can be categorised into two types: midpoint and endpoint impact indicators.

Midpoint impact indicators are classified based on the similarity of environmental effects from various elementary flows. For instance, elementary flows that cause acidification in soil are grouped together under the category of terrestrial acidification. Typical midpoint impacts include climate change, ozone depletion, acidification, eutrophication, photochemical ozone formation, ecotoxicity, human toxicity, particular matter formation, ionising radiation, land use, water use, and abiotic resource use. Emerging categories like biotic resource use, noise, and pathogens, may become more essential in the future.

Endpoint impact indicators are groups of various midpoint impact indicators. They represent Area of Protection (AoP) that encompass human health, ecosystem quality or natural environment, and natural resources and ecosystem services. In some assessment methods, such as IMPACT 2002+, the climate change midpoint impact indicator is considered equivalent to the global warming endpoint impact indicator since there are no other relevant midpoint impact indicator to be grouped under this endpoint impact indicator.⁹⁴ These impact indicators are reported as quantitative scores, either in their own units or through normalisation. The outcomes of the impact assessment should be used as supporting information and not as the sole answer to the research question. Environmental impact

scores should be interpreted by the practitioner to fulfil the goals that were set at the beginning of the study.

While LCA is often employed to assess environmental impacts in industrial-scale processes, it is equally valuable for evaluating laboratory-scale processes. In the context of developing innovative synthesis methods, LCA enables the assessment and comparison of environmental impacts between traditional and novel approaches. This analysis can pinpoint hotspots in the process that may need further improvement. Ultimately, the insights gained from LCA assessment serve as a valuable reference for evaluating the environmental sustainability of scaling up the process.

1.4. Deep eutectic solvent (DES): Benign alternative for continuous synthesis of HCP

Having established the importance of sustainable practices in chemical processes, a promising benign alternative with significant potential to advance the sustainability of continuous flow synthesis of HCPs should also be explored, especially in the climate current, where there is a transition to Industry 5.0. According to Anastas' 'Twelve Principles of Green Chemistry', one key principle for achieving clean chemical technology is to perform less hazardous synthesis.⁹⁵ In HCP synthesis, a major portion of chemical consumption is attributed to the solvent. DCE, widely used in Friedel-Crafts alkylation, is classified as highly hazardous, by various solvent selection guides – Provide their names and references, primarily due to its carcinogenic property.^{96, 97} Other solvents used in HCP synthesis include dichloromethane,^{12, 44} chloroform,³⁰ carbon tetrachloride.³ These solvents share similar hazardous rankings with DCE.⁹⁷ Seeking an alternative solvent holds the potential to significantly enhance the sustainability of HCP synthesis.

The development of a new class ionic liquids, known as deep eutectic solvent (DES),⁹⁸ has expanded the boundary of Friedel-Crafts reactions.⁹⁹ DES is formed by mixing two solid components: an ammonium salt and a hydrogen bond donor.⁹⁸ The presence of the hydrogen bond donor reduces the lattice energy of the system, resulting in a lower freezing point. This allows the system to remain a fluid state at a temperature lower than the original melting point of each component (Figure 5).¹⁰⁰ The choice of these components indicates the toxicity level. Choline chloride (abbreviated as ChCl in this thesis), a common ammonium salt used in DES, is biodegradable, has low-toxicity, and widely used as a pro-vitamin for livestock. It is also abundant and inexpensive.¹⁰⁰ The selection of the hydrogen bond donor varies based on reaction design, offering varying strengths of bonding with ChCl, influencing the extent of freezing point depression. The toxicity level of DES also depends on the component used as the hydrogen bond donor. For example, chlorometallate salts exhibit a greater depression of freezing point than alcoholic hydrogen bond donors, however, they contain hazardous elements that necessitate additional solvent extraction to separate these metals before disposal.¹⁰¹

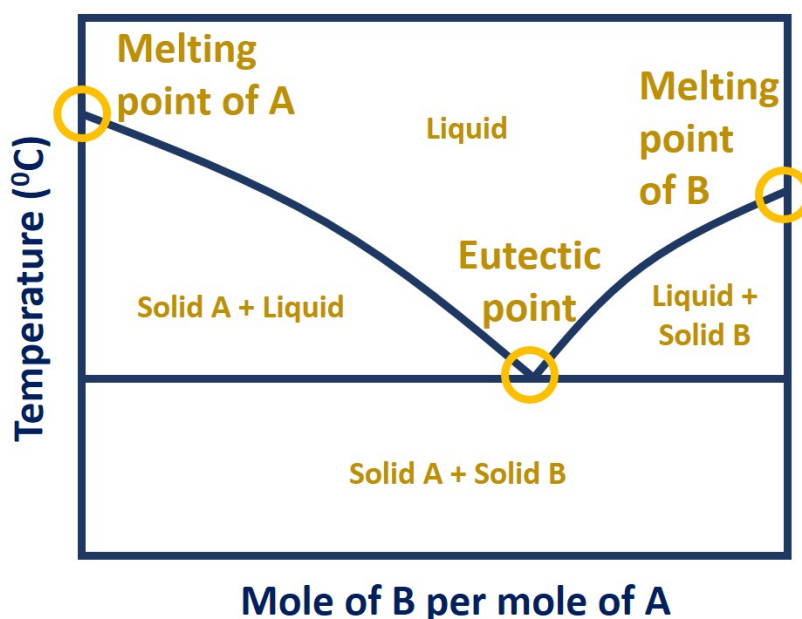


Figure 5 Eutectic system

The utilisation of DES derived from ChCl and ZnCl_2 has recently found application in Friedel-Crafts acylation.⁹⁹ DES serves as a dual-function component in the system, functioning both as a catalyst and a benign solvent simultaneously. An investigation into the utilization of $[\text{ChCl}]_m[\text{ZnCl}_2]_n$, where m referred to molar ratio of ChCl ranging from 0 – 1 and n referred to molar ratio of ZnCl_2 ranging from 1 – 3, in Friedel-Crafts acylation of anisole and indole with propionic anhydride under microwave irradiation has revealed a correlation between the molar ratio of ZnCl_2 and reaction conversion. The results demonstrated that the conversion of reactions from both anisole and indole improved by 25 % and 4 %, respectively, when substituting ZnCl_2 with $[\text{ChCl}][\text{ZnCl}_2]$. Furthermore, this improvement increased by 100 % and 60 %, respectively, when substituting ZnCl_2 with $[\text{ChCl}][\text{ZnCl}_2]_3$. These findings highlight the enhancement in reactivity when DES is employed instead of pure ZnCl_2 and the improvement in reactivity corresponding to the molar ratio of the catalyst. Given that HCP synthesis follows the principle of Friedel-Crafts reaction, the application of DES for HCP synthesis *via* a continuous flow system is a promising area for investigation.

1.5. Mechanochemical synthesis: Alternative method for HCP continuous synthesis using DES

In addition to the main investigation into the implementation of a continuous flow system for HCP synthesis, an alternative approach to continuous HCP synthesis using DES as a more benign solvent, continuous mechanosynthesis, has been proposed in this study. Mechanochemistry synthesis involves grinding solid monomers and catalysts, initiating chemical reactions through mechanical force.¹⁷ A typical setup for mechanosynthesis is ball milling. This is an autonomic grinder in the form of a vessel reactor filled with several milling balls. The grinding motion could be in a one-plane motion, *i.e.*, from side to side using shaker or vibration mills, or it could be spun rotationally using the planetary mills (Figure 6).¹⁰² Planetary mills have already been successfully applied for the synthesis of internally

crosslinked p-BCMBP through liquid-assisted grinding, utilising FeCl_3 and diethyl ether as catalyst and liquid additive. The resulting HCP was achieved within 35 minutes and possessed a BET surface area of $1720 \text{ m}^2 \text{ g}^{-1}$.¹⁰³ External crosslinking using FDA as a crosslinker was also attempted using ball milling technique, obtained HCPs with a BET surface area of $784 \text{ m}^2 \text{ g}^{-1}$ with a product yield close to 100 %. While the ball milling technique excels in productivity and produces a high BET surface area for the synthesised HCPs, the major disadvantage involves with the discontinuity of the synthesis process, hindering scalability to multi-kg scale manufacturing of HCPs.

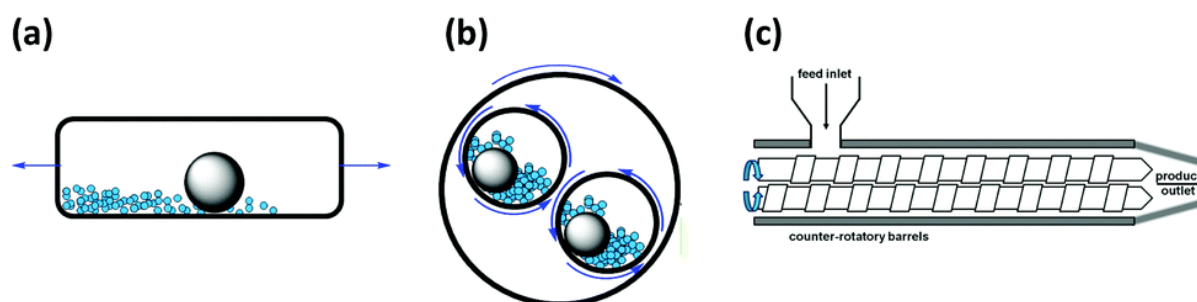


Figure 6 Mechanochemical tools and instruments: a) shaker or vibration mills, b) planetary mills, c) twin screw extruder¹⁰²

A continuous approach for mechanosynthesis is twin screw extrusion (TSE) (Figure 7 in Chapter 6).¹⁰⁴ TSE is a process generally employed for polymer blending on an industrial scale.¹⁰⁵ The system consists of two parallel screws that can either co- or counter-rotate inside a cuboid barrel. (Figure 7) A feed port allows solid particles, such as polymer resins, to enter the barrel. The equipped heating system throughout the barrel allows the resins to melt, while the rotating screws facilitates blending and transporting the feed mixture along the barrel. The implementation of TSE as a replacement for ball milling has been studied for the fluorination reaction.¹⁰⁶ The study demonstrated an improvement in productivity, measured in terms of STY, as it increased by a factor of 100 compared to ball milling, reaching an STY of $3395 \text{ kg m}^{-3} \text{ day}^{-1}$. Mechanochemistry through TSE also upscales metal organic frameworks synthesis. ¹⁰⁴Commercially significant metal organic frameworks, such as ZIF-8, was synthesised in solvent-free conditions, achieving a STY of up to $144 \times 10^3 \text{ kg m}^{-3} \text{ day}^{-1}$, a 100-fold increase over conventional batch metal organic frameworks synthesis.

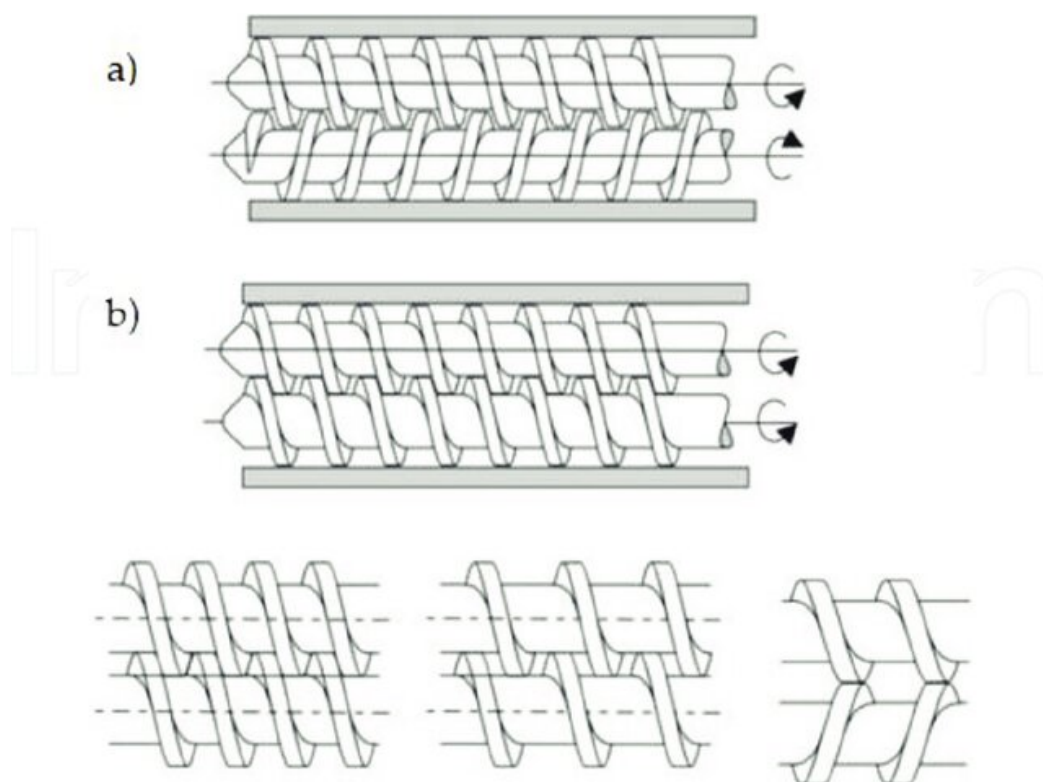


Figure 7 a) Counter rotation and b) Co-rotation configurations of twin screw extruder ¹⁰⁷

In theory, solvent-free mechanosynthesis of HCP through TSE is feasible and expected to yield completely crosslinked HCP product, as it operates on the same principle as ball milling. However, it should be noted that lab-scale extruders are made from stainless-steel,¹⁰⁸ which is not suited for direct contact with the catalysts such as FeCl_3 deployed in Friedel-Crafts reactions as it can corrode the extruder material. Therefore, the pursuit of solvent-free mechanosynthesis of HCP may require an extruder made from zirconium oxide, the same materials used in the batch vessel and milling balls. Meanwhile, mechanosynthesis of HCP using DES as a more benign solvent offers a promising alternative. Batch synthesis of HCPs using DES demonstrated that a mixture of ChCl and ZnCl_2 can facilitate the crosslinking reaction. Inspired by these recent progresses, this work seeks to evaluate the feasibility of synthesizing HCPs using DES as solvents *via* TSE to simultaneously improve both the productivity and sustainability of HCP synthesis.

1.6. Aims of the thesis

In response to the escalating global demand for HCPs alongside the growing environmental concerns, this study centres on the pivotal goal of intensifying the HCP synthesis process. By doing so, the research seeks to boost productivity and sustainability, thereby laying the groundwork for large-scale manufacturing in the future.

The primary aim is to develop an innovative continuous flow system for HCP synthesis, surpassing the limitations of conventional batch methods. This shift towards the intensified synthesis process is poised to enhance productivity and sustainability, making it a viable protocol for potential large-scale production to meet the burgeoning global demand for HCPs while reducing the impacts toward environment. Furthermore, an integral aspect of this

intensification effort includes attempting green synthesis practices, aligning with the broader goal of environmental responsibility.

It is important to emphasise that while this research represents a significant step toward the production at the industrial level, the work has yet to reach the stage of full-scale production. Rather, this laboratory-scale experimentation serves as a protocol for future industrial implementation. The long term goal is to position HCP production to meet the global demand effectively once it reaches that magnitude, all while considering and mitigating environmental impacts.

1.7. Objectives of the thesis

The objectives of this thesis are structured into four distinct parts, as illustrated in Figure 8.

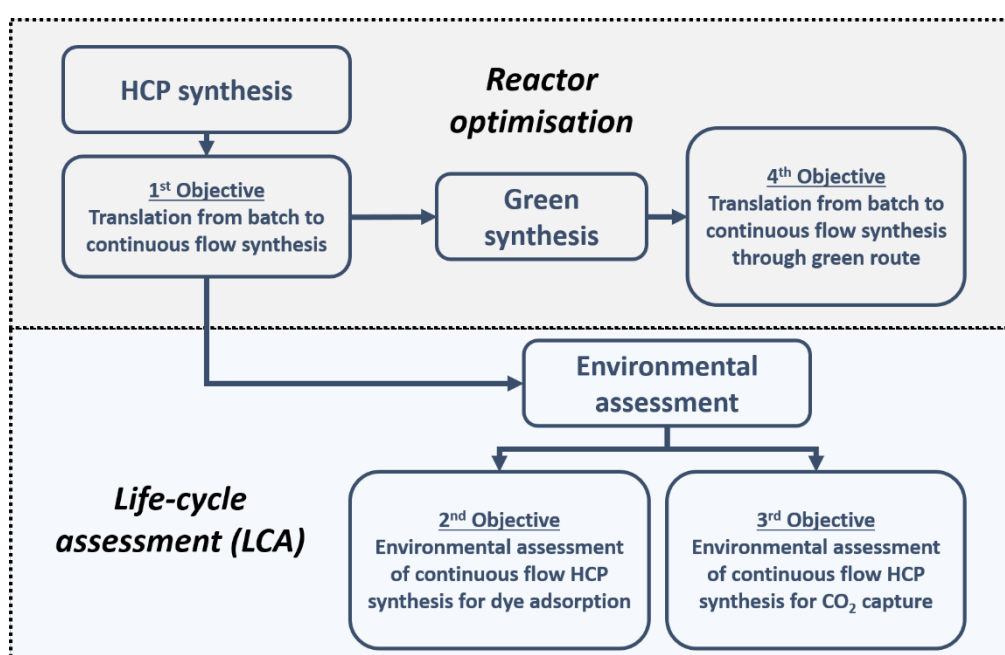


Figure 8 Objectives and workflow of this study

The first objective is to incorporate an in-house designed continuous flow reactor into the HCP synthesis process. Three types of HCPs, corresponding to three chemical synthetic strategies, are synthesised through this continuous flow reactor to showcase the versatility of flow synthesis. These three HCPs are also synthesised using batch reactions under identical reaction conditions to provide a benchmark. Following optimisation of the flow process for each HCP type, the resultant products are characterised to assess their textural properties, *i.e.*, BET surface area and pore size distribution, and their molecular structures. Both batch- and flow-synthesised HCPs are subjected to CO₂ and N₂ adsorption tests to evaluate their performance capacity and CO₂ selectivity over N₂. The goal of this objective is to demonstrate the influence of continuous flow synthesis on the quality of HCP products, including textural characteristics and performance properties, as well as its impact on process productivity. Findings from this objective is used to validate the potential of flow synthesis as an alternative scale-up method for HCP manufacturing.

The second objective is to evaluate the environmental impact of lab-scale continuous flow HCP synthesis, particularly in the context of dye adsorption applications. Dye adsorption experiments are conducted using two different dye types to collect separation performance data from both batch and flow HCP syntheses. An environmental impact assessment is conducted using the LCA methodology, quantifying environmental impacts across various categories. Environmental impact scores resulting from HCP synthesis *via* flow are compared with scores from HCP batch synthesis. This objective seeks to identify major environmental impact hotspots for each synthesis method and ascertain whether flow synthesis is more environmentally sustainable than batch synthesis for the removal of two dye types. The results of this study underscore the environmental benefit of implementing flow system into HCP synthesis for future manufacturing scale-up.

The third objective of the study corresponds to the gas adsorption data obtained from the first objective. Given that the synthesis method was found to influence CO₂/N₂ selectivity, this study intends to use LCA to determine whether the excellent CO₂/N₂ selectivity observed in one of the HCPs synthesised using the continuous flow method would result in a reduced requirement of HCP for CO₂ capture, subsequently leading to lower environmental impacts compared to batch synthesis. The third objective follows a similar approach to the second objective of study. It involves performing a similar LCA modelling procedure, but with the reference basis of adsorbed CO₂ instead of adsorbed dye molecules. The benchmarking process against HCP batch synthesis is executed similarly to the previous study. The assessment based on the adsorption of 40 mg of CO₂ at 1 atm and 298 K. Due to the different textural properties and performance capabilities between flow- and batch-synthesised HCPs, the required amounts of HCPs differ between the two methods, resulting in different environmental impacts. This objective highlights the environmental advantage of the flow system in various applications, irrespective of the specific application.

The last objective explores transforming the sustainability of HCP synthesis in flow reactors. This is achieved by implementing continuous synthesis methods using a more benign alternative which is DES. However, transporting DES in a regular continuous flow system poses challenges as DES can exist in both solid and liquid states depending on temperature. This objective is divided into two projects, each corresponding to using the flow reactor developed in the first objective and TSE continuous flow synthesis of HCPs using DES.

In summary, this study endeavours to develop a practical continuous HCP synthesis protocol applicable to future manufacturing scale processes. The proposed flow synthesis aims to produce higher-quality HCPs, enhance productivity, and reduce environmental impacts compared to batch synthesis. This study will provide valuable insights into the feasibility, advantages, and environmental sustainability of continuous synthesis for HCP production, paving the way for potential advancements in the field.

2. Experimental

The characterisation techniques involving in this study are summarised in Table 1. The table includes the purpose of the characterisation and the chapters in which these techniques were presented. The details of the principles of each characterisation technique was described in the following section.

Table 1 Characterisation techniques using in this study

Characterisation techniques	To determine...	Used in chapter...
BET analysis (+ DFT method)	Specific surface area & Pore size distribution	3, 6
FTIR spectroscopy	Molecular structure	3
¹³ C NMR spectroscopy	Molecular structure	3, 6
TEM	Surface morphology	3
UV-VIS spectroscopy	Dye concentration in solution	4

2.1. BET measurement

BET theory is the principal method to determine the specific surface area of hypercrosslinked polymers in this thesis. This theory extends from the Langmuir theory, addressing the possibility that the adsorption of gas by the solid sample could be multi-layered, not just mono-layered.¹⁰⁹ Because the specific surface area is determined through the surface site where adsorbates, *i.e.*, N₂ gas can be occupied, the BET surface area provides more accuracy than the Langmuir surface area.

The apparatus used for BET measurement is called physisorption analyser. In this analyser, the sample is exposed to high-purity gas at its boiling point temperature. The common gas used for BET analysis of porous organic polymers is N₂.¹¹⁰ After a degassing stage to remove any adsorbed residue species in the adsorbent sample, the solid sample is then soaked in liquid N₂ at 77 K. The analysis is run at various pressure, from low to high, to record the adsorption isotherm. The variation in pressure is equivalent to the concentration, which influences the volume of adsorbed gas following the assumption in the Langmuir theory. After reaching the saturated pressure, the gas desorption is recorded as the pressure is gradually decreased to complete the characterisation cycle.¹⁰⁹ Thus, the sorption isotherm consists of both adsorption and desorption isotherms.

The sorption isotherm is a plot of adsorbed gas volumes against relative pressure. The shape of the isotherms, along with the hysteresis loop created between adsorption and desorption data, can provide an estimation of the pore and structure of the studied adsorbent. Currently, there are six types of physisorption isotherms and five main types of hysteresis loops classified by IUPAC.¹¹¹ It is possible to have a mixed type of isotherm, indicating a mixed pore architecture.³³

The calculation of the multi-point BET surface area is explicitly based on the adsorption data.¹⁰⁹ A linear plot between the left-hand side of BET equation (Equation 1) and the relative pressure is required to obtain the values of the intercept and slope of the BET equation. From

these two values, the maximum adsorbed gas volume and the BET constant are determined, and consequently, the BET surface area is calculated using Equation 2. The accuracy of the BET surface area was developed specifically for microporous material by applying Rouquerol criteria during data selection.¹¹² These criteria were proposed to ensure the appropriate pressure range. There are four criteria to be considered, as following:

- 1) The BET constant, *i.e.*, C is always a positive value
- 2) The selected data range should not exceed where $Q(1 - \frac{P}{P_0})$ starts to decline
- 3) The pressure corresponding to Q_m should be in the selected pressure range
- 4) The difference between the pressure corresponding to Q_m and $1/(\sqrt{C} + 1)$ should not exceed 10%

Equation 1 BET equation for specific surface area determination

$$\frac{1}{Q(\frac{P_0}{P} - 1)} = \frac{1}{Q_m C} + \frac{C - 1}{Q_m C} \left(\frac{P}{P_0} \right)$$

Q : Adsorbed gas volume

Q_m : Maximum adsorbed gas volume to form a monolayer

P/P_0 : Relative pressure

C : BET parameter

Equation 2 Multi-point BET surface area calculation

$$BET \text{ surface area} = \frac{Q_m L_{av} A_m}{M_v}$$

L_{av} : Avogadro's number (The exact value of $6.02214076 \times 10^{23}$ reciprocal moles)

A_m : Cross-sectional area of the adsorbate ($16.2 \text{ \AA}^2$ for a nitrogen molecule)

M_v : Molar volume (22.414 L at STP)

Gas adsorption at different pressure regions can also provide information about the distribution of pores based on their size. According to the IUPAC classification, pore width is categorised into three ranges: micropores ($< 2 \text{ nm}$), mesopores ($2 - 50 \text{ nm}$), and macropores ($> 50 \text{ nm}$).¹¹¹ This distribution can be graphically represented as the pore size distribution by plotting the differential pore volumes against pore width. The most well-known and reliable method for obtaining pore size distribution in porous materials is density functional theory (DFT).^{111, 113} Although several DFT-based methods are still under development,¹¹⁴ classical DFT is the chosen method in this thesis.

2.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectroscopy is used to identify the molecular structure of a sample because each type of material possesses its own unique spectrum. The spectrum of the sample records either the transmittance or the absorbance (the inversion of the transmission) of the infrared

radiation percentage after it passes through the sample.¹¹⁵ Different types of bonds absorb infrared beams at different frequencies, so the peaks representing different bonds are reported at different wavenumbers in the IR region. The same principle applies to the vibration pattern, *for e.g.*, stretching, bending, rocking of bonds, as the infrared beam induces these vibration patterns at different frequencies.¹¹⁵ Figure 1 shows the range and intensity of the peaks corresponding to common functional groups in molecules. The benefits of using FTIR spectroscopy are that the preparation step is simple and the samples are not destroyed or deteriorated. It requires less time to perform compared to other spectroscopies.¹¹⁶

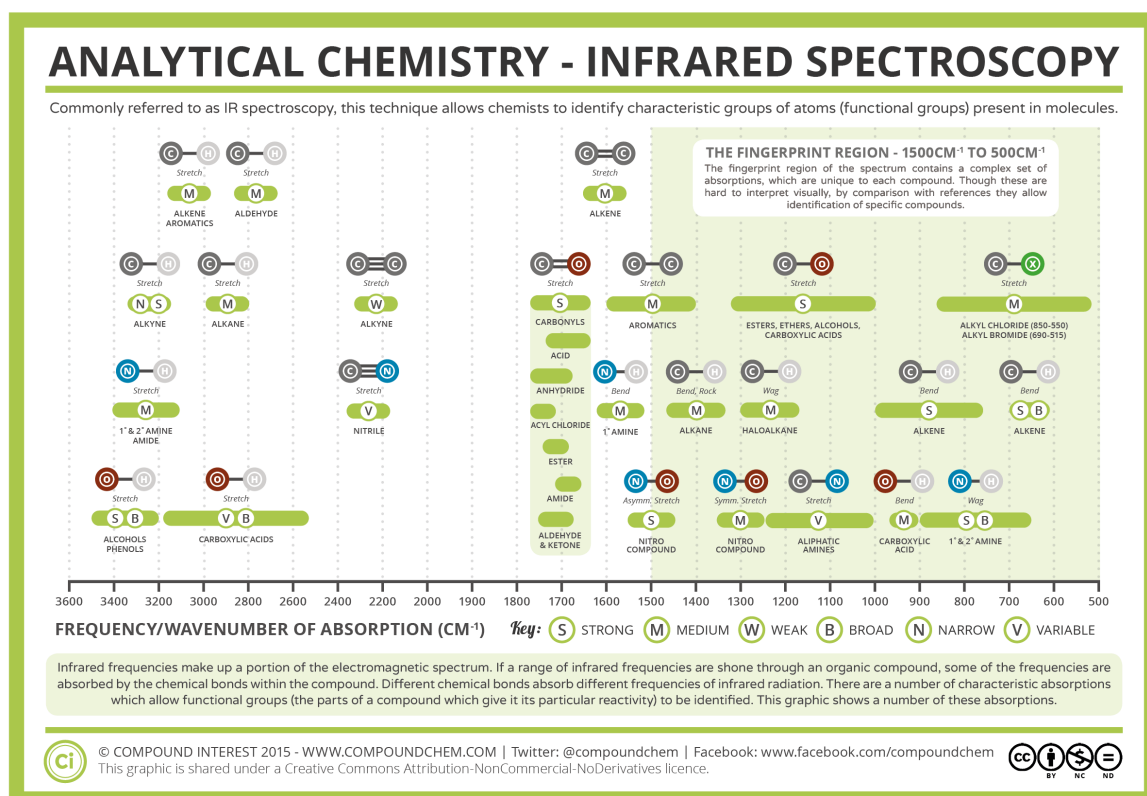


Figure 1 Reference chart of FTIR spectra for the common functional groups (Figure reference: CompoundChem.com)

2.3. Carbon-13 nuclear magnetic resonance (¹³C-NMR) spectroscopy

¹³C-NMR spectroscopy is another characterisation method used to distinguish the molecular structure of the sample, specifically for carbon-contained materials like HCP. This method is based on the detection of ¹³C spinning, which act as small magnets when placed in an external magnetic field. These spins can either align with the magnetic field or against it. The spectrum is recorded when the spins are against the magnetic field. Since the characterisation involves the ¹³C isotope, which accounts for 1 % of all carbon in nature, the interpretation of the spectra is relatively simple compared to ¹H-NMR spectroscopy.¹¹⁷ Figure 2 shows the range and intensity of the peak corresponding to common functional groups in molecules.

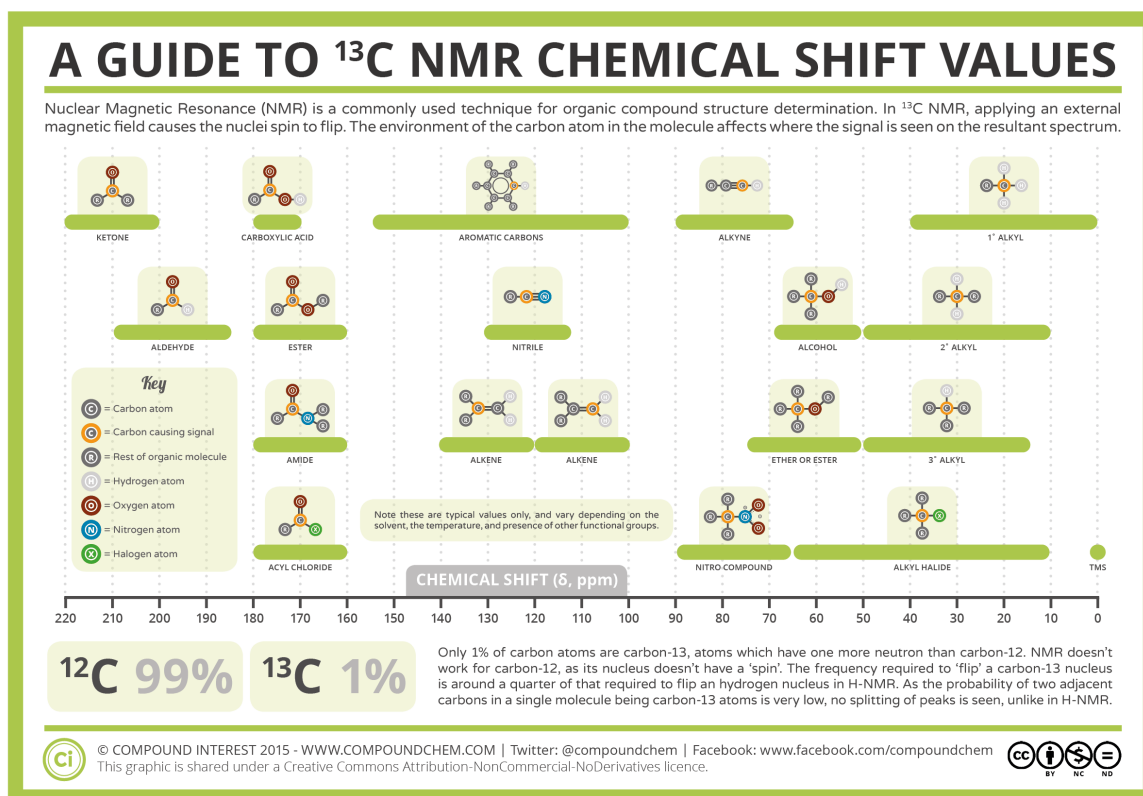


Figure 2 Reference chart of ^{13}C -NMR spectra for the common functional groups (Figure reference: CompoundChem.com)

2.4. Transmission electron microscopy (TEM)

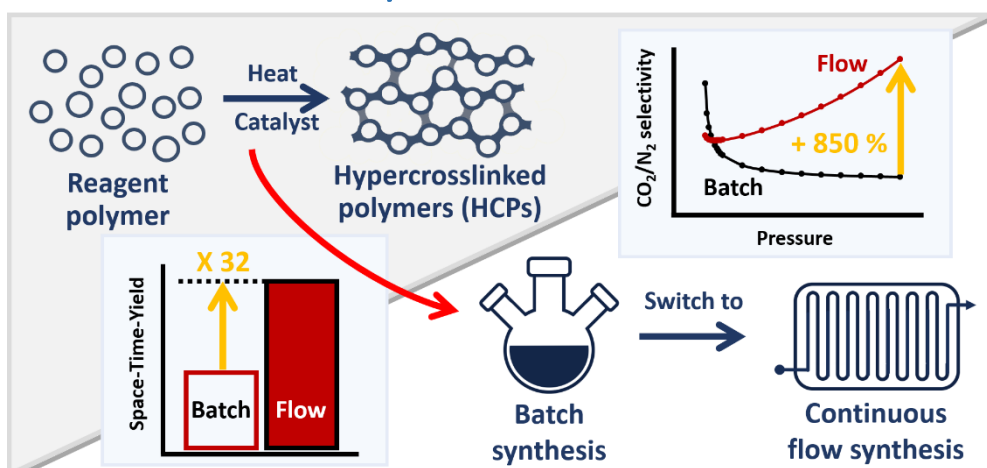
TEM is the electron microscope used to inspect the morphology of a sample. The principle relies on the beaming of electrons passing through an image-producing system, consisting of condenser lens, a specimen layer, objective aperture lens, intermediate lens, and projector lens. The electron image is then converted into a form that is perceptible to the human eye through the image-recording system, comprising a fluorescent screen and a digital camera.¹¹⁸ Typically, TEM is employed to inspect the morphology of crystallised structures. However, for the structure of HCPs, which are amorphous, the microscopic images of HCPs are not as clear, and microporous structure is not obviously presented.

2.5. Ultraviolet-visible (UV-VIS) spectroscopy

UV-VIS spectroscopy is employed to determine the concentration of dye solutions after they have been adsorbed by HCPs synthesised in this work. The dye concentration is correlated to the light absorbance detected through this characterisation technique. Before determining the unknown concentration of the studied dye solution, a calibration curve, *i.e.*, linear equation must be established. The calibration process involves conducting UV-VIS spectroscopy on various known concentration of the studied dye, along with a blank solution, which is usually the solvent of the system, such as DI water in this case. From the UV-VIS spectra (absorbance vs. wavelength), the absorbance values at the highest absorbed wavelength are plotted against the concentration of the solution. A good calibration curve

should exhibit a linear trend. The mathematical formula derived from this plot can then be applied to determine the concentration of same dye solutions. This is accomplished by substituting the absorbance value of the wavelength of maximum absorption for the solution of the same dye type with unknown concentration into the equation. Through this process, the concentration can then be accurately ascertained.¹¹⁹

3. Continuous flow synthesis of HCP



Graphical abstract - Translation of HCP synthesis from batch to continuous flow synthesis

3.1. Introduction

As per the majority of literature on HCP synthesis, crosslinking reactions in batch system typically demand prolonged reaction times. These reaction durations can vary from several hours²⁴ to multiple days.¹⁸ Even the production of commercially available Macronet series HCPs relies on batch tanks, requiring 3 - 12 hours of mixing and heating in DCE at 80 °C.⁵⁶ It is worth noting that the standard reaction time for HCP synthesis stands at 24 hours. Recognising this, a proposition to significantly reduce reaction times emerged by replacing traditional batch synthesis with a novel continuous flow synthesis approach. This approach has already found success in expediting the synthesis of other microporous materials, such as polymers of intrinsic microporosity synthesis, where reaction times were reduced by 90 %.¹²⁰ The immediate benefit of this reduction in reaction time lies in its potential to enhance HCP synthesis productivity, positioning it to meet the ever-expanding global demand.^{23, 121}

An innovative continuous flow system for HCP synthesis was introduced in 2019.³⁰ This approach was applied to the synthesis of triptycene-based HCP, showcasing its potential as an alternative synthesis apparatus for HCP production. This continuous flow system led to a reduction in reaction time, allowing the synthesis of 2 g of HCP in 2 hours, a remarkable improvement compared to the 24 hours requirement in batch synthesis. However, during the preliminary experiments, there was a hypothesis that solid catalyst FeCl₃ might pose challenges related to clogging. To overcome this challenge, FeCl₃ was substituted with trifluoromethanesulfonic acid (TfOH), a liquid Bronsted acid. It is essential to highlight that Bronsted acid is regarded as one of the strongest acids,¹²² and can cause significant health risks, including severe burns and respiratory irritation.¹²³ However, the issue of clogging within the system might not be solely attributed to the presence of a solid catalyst. Instead, it might be a consequence of the solid formation arising from the crosslinking reaction itself. This new perspective set the stage for this current study, aiming to develop a comprehensive understanding of the continuous flow HCP synthesis process through optimisation. The system of this study maintained the utilising of the common FeCl₃ catalyst, instead of the harsh TfOH. Our key focus was to identify the optimal operating conditions to achieve the

desired synthesis outcomes, including higher productivity compared to batch synthesis and a high specific surface area of the product.

The scope of this study delved into the optimisation of four operating parameters: residence time, precursor feed concentration, reagent ratio, feed flow rate, and operating temperature. Recognising the variation of these parameters in tailoring the synthesis of various HCP species, three types of HCP corresponding to three synthetic approaches were synthesised to showcase the versatility of the continuous flow reactor. The first HCP type, poly-dichloro-*p*-xylene, represented internally crosslinked HCP. The second, polystyrene crosslinked with DCX, represented post-crosslinked HCP. Lastly, polystyrene crosslinked with FDA represented externally crosslinked HCP. These flow-synthesised HCPs were benchmarked against their batch-synthesised counterparts, comparing BET surface area and pore size distribution. These properties provided insights into their performance in CO₂ and N₂ adsorption and CO₂/N₂ selectivity. Crucially, this study showcased the increase in productivity of flow synthesis compared to batch synthesis. The STY was employed as productivity indicator. Following these investigations, the results of this study could impact the potential to adopt continuous flow techniques in the manufacturing-scale production of HCP.

3.2. Discussion highlight, limitations, and conclusions

The successful synthesis of HCP using a continuous flow reactor had yielded significant improvements across various aspects. By transitioning from the batch reactor to the continuous flow reactor, the surface area-to-volume ratio of the reactor was increased by 68 fold, leading to enhanced heat transfer rates. Furthermore, the smaller volume of the continuous flow reactor resulted in shorter diffusion pathways, thereby enhancing mass transfer rates. This cumulative effect improved reaction kinetics, leading to shorter reaction times. Under the optimal operating conditions for internal, post-, and external crosslinking approaches, reaction times were reduced to 5, 10, and 15 minutes, respectively, from the initial 24 hours. This substantial reduction in reaction time translated to a remarkable enhancement in productivity, as evident in the 32, 117, and 68 fold increase in STY for internal, post-, and external crosslinking, respectively. Flow-synthesised HCPs exhibited BET surface areas of 950, 816, and 1092 m² g⁻¹ for internal, post-, and external crosslinking, respectively, slightly lower by 1.5 %, 9.6 %, and 6 % compared to HCPs synthesised using the batch method. Notably, internally crosslinked HCPs (p-DCXs) obtained from the flow synthesis process showed a substantial increase in micropore volume by 569 %, contributing to a CO₂/N₂ selectivity of 71.5, representing an 850 % enhancement in selectivity. This underscores the advantages of the continuous flow system in synthesising HCPs with enhanced textural property.

A noteworthy aspect of this work involved exploring the influence of the four operating parameters on the microporosity of flow-synthesised HCPs, with a focus on the external crosslinking approach. The optimal residence time, leading to a Reynolds number of 65 (close to the optimal Reynolds number of 40 in the helical coil), resulted in optimal mixing intensity and a notable 595 % increase in micropore volume over a 15-minute reaction time. Further

crosslinking duration could result in excessive crosslinking, potentially leading to a decrease in BET surface area due to smaller pore size than the kinetic diameter of adsorbed N₂ gas. The polystyrene to FeCl₃ to FDA ratio also played a significant role in micropore generation, with an increase in the weight ratio from 1:3:3 to 1:5:5 resulting in a 1493 % increase in micropore volume, attributed to the increase amount of catalyst and crosslinker in the reaction. Elevating the temperature parameter by 10 K resulted in an 84.8 % enhancement in micropore volume, indicating the sensitivity of the process to temperature variations. In contrast, substrate concentration had the least significant effect on microporosity. An increasing the PS concentration from 0.4 % to 0.6 % led to a modest 37.5 % increase in micropore volume. Further increases in concentration did not yield significant changes, suggesting that the synthesis of HCP is not highly sensitive to this parameter.

For further suggestion, the scope of the study could be expanded to explore a broader range of parameters potentially affecting the crosslinking process in a continuous flow reactor. Investigating the influence of reactor specifications such as tube cross-section diameter, pitch length, and tube wall thickness could enhance the degree of mixing, resulting in higher product yields of flow-synthesised HCPs. This, in turn, could lead to enhanced STYs and reduced chemical consumption. However, modifying multiple reactors for trial-and-error testing would require substantial materials. To address this challenge, computational modelling tools like COMSOL could be employed to gain insights into fluid behaviour in different reactor designs prior to conducting physical experiments. This approach could help identify promising reactor configurations and guide the experimental optimisation process. A current limitation to this approach is the lack of kinetic data on the crosslinking process. Gathering accurate and comprehensive kinetics data would be valuable for a deeper understanding of the reaction mechanism and further process optimisation.

This study has demonstrated the benefits of continuous flow synthesis in enhancing microporosity of HCPs and process productivity. The findings suggest that further exploration of the flow system for production upscaling could yield additional advantages for the commercialised sectors. However, it is important to acknowledge that the study did not encompass the assessment of environmental aspects of the continuous flow synthesis approach in comparison to the batch system. Given the significance of environmental considerations alongside economic value, future research should focus on evaluating the environmental impact of the flow synthesis approach. This would provide a comprehensive understanding of the sustainability and potential environmental benefits of implementing flow synthesis in HCP production.

PAPER

View Article Online
View Journal | View IssueCite this: *J. Mater. Chem. A*, 2023, **11**, 9859Flow synthesis of hypercrosslinked polymers with additional microporosity that enhances CO₂/N₂ separation†Nadhita Chanchaona,^a Liang Ding,^a Shiliang Lin,^a Sulaiman Sarwar,^a Simone Dimartino,^a Ashleigh J. Fletcher,^b Daniel M. Dawson,^c Kristina Konstas,^d Matthew R. Hill^d and Cher Hon Lau^{*a}

Hypercrosslinked polymers (HCPs) are typically synthesised over 24 hour batch reactions, limiting productivity rates during scale-up production. Continuous flow synthesis can potentially overcome this limitation. However, the formation of insoluble HCP products, compounded by HCP expansion due to solvent adsorption during synthesis can clog flow reactors. Here, we overcome clogging issues through reactor design and optimisation of synthesis parameters. Using this reactor, we synthesised HCPs via internal, post-, and external crosslinking strategies underpinned by Friedel–Crafts alkylation over various synthesis parameters – residence time, substrate concentration, reagent ratio, and temperature. The space-time-yield (STY) values, a key parameter for productivity rates, of flow synthesis were 32–117 fold higher than those in batch reactions. HCPs produced via internal crosslinking in flow synthesis contained additional microporosity that enhanced CO₂/N₂ selectivity at 298 K by 850% when compared to HCPs produced in batch reactions. Outcomes from this work could enable high productivity scale-up production of HCPs for post-carbon capture.

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Introduction

Hypercrosslinked polymers (HCPs) are excessively crosslinked, amorphous polymers typically synthesised via Friedel–Crafts alkylation (Fig. 1). In this reaction, aromatic protons are replaced with methylene bridges that are linked to an adjacent aromatic molecule. This is facilitated by an electrophilic attack on the aromatic ring by a carbocation. This can be achieved by post-, internal, and external crosslinking.¹ Post-crosslinking uses halogenated crosslinkers to link up the chains of polymers such as polystyrene or polystyrene-*co*-divinylbenzene. Internal crosslinking is akin to a condensation reaction in which halogenated compounds are crosslinked. External crosslinking exploits formaldehyde dimethyl acetal (FDA) as the crosslinker to link up simple aromatic compounds.² During the crosslinking process, solvent molecules pre-occupy the free spaces between the newly linked up polymer chains. Removing

solvent molecules from the product by drying leads to the formation of porous architectures that underpin Brunauer–Emmett–Teller (BET) surface areas as high as 2000 m² g^{−1}.³ As such, HCPs are widely deployed in the industry as ion-exchange resins⁴ such as Purolite's Macronet™,⁵ DowDupont Inc.'s Amberlite™, and Lanxess AG's Lewatit® series, and potentially for gas storage and separations.^{6,7} The global market value of HCPs in 2020 was USD\$1.4 billion and is expected to reach USD\$2 billion by 2028.⁸

Most HCPs are produced via batch reactions over 18–24 hours⁹ to ensure extensive crosslinking¹⁰ and this may be inadequate to produce enough HCPs to meet the growing global demand. In the first hour of batch reactions, more than 80% of the reagents are used up in cross-linking. The pores of the initial polymer will adsorb solvent molecules, creating a gel-like structure. More solvent is then added to disperse the initially-

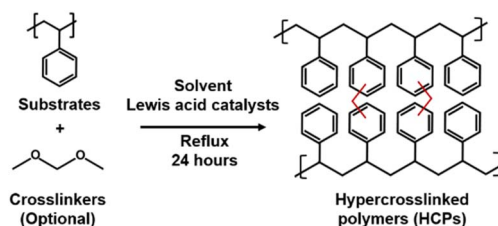
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Fig. 1 Generic Friedel–Crafts alkylation for HCP synthesis.

formed polymers, breaking up the gel-like material to ensure complete crosslinking.

Most studies in this field are focused on developing new HCP materials with unprecedented adsorption capacity,^{11,12} identifying alternative reagents (solvents, monomers) for the sustainable synthesis of HCPs,¹³ and improving batch productivity rates.¹⁴ For example, low HCP productivity rates production can be improved by reducing synthesis time from 24 hours to 5–35 minutes *via* solvent-free mechanochemical ball milling and liquid-assisted grinding.¹⁵ This significant reduction in synthesis duration does not impact HCP quality, with specific surface areas reaching 625–1720 m² g^{−1}. Another technique suitable for improving the productivity of HCP production is flow synthesis.

The key benefit of replacing batch reactions with flow synthesis is improving productivity rates. To date, flow chemistry had been used for synthesising microporous materials, such as polymers of intrinsic microporosity (PIM),¹⁶ metal-organic frameworks (MOFs),¹⁷ covalent organic frameworks (COFs),¹⁸ and HCPs.¹⁰ Flow syntheses of MOFs and COFs enhanced the space-time yield (STY) – a key indicator of productivity rates, comprising product yield, operating time, and reactor volume,¹⁷ by 30 fold,¹⁹ and 94 fold,¹⁸ respectively. These significant STY improvements were attributed to a reduced production time. Meanwhile, Fritsch deployed continuous flow reactions to reduce the PIM synthesis time by 90%.¹⁶ The first reported example of flow synthesis of HCPs was reported in 2000 when Vincent and co-workers reported using a tubular reactor to control the particle size of HCPs formed *via* post-crosslinking during suspension polymerisation.²⁰ However, this work mainly focused on narrowing the particle size distribution. Our group previously deployed flow synthesis to produce HCPs *via* the external crosslinking method.¹⁰ A key limitation of this proof-of-concept was reactor clogging by the newly formed insoluble HCP products that expanded upon solvent adsorption within the reactor.

In this work, we overcome reactor clogging by optimising reactor design and synthesis parameters – residence time, temperature, reagent concentration, and ratio for flow synthesis of HCPs *via* internal crosslinking of α,α' -dichloro-*p*-xylene (DCX), post- and external crosslinking of waste Styrofoam in a bespoke coil reactor. To demonstrate the effects of flow synthesis on HCP quality and productivity rates, we compared the specific surface areas, micropore volumes, and STY value of HCPs produced from the flow synthesis with batch reactions. Results from this work support the theory that flow synthesis could be used to scale the production of good-quality HCPs. This is different from existing approaches that rely on HCP functionalisation,^{21–23} utilisation of bespoke²⁴ or novel^{25,26} monomers in HCP synthesis, and modified synthesis protocols.¹⁵ Our approach establishes a new method to tailor and enhance HCP CO₂/N₂ selectivity *via* reactor design and flow synthesis.

Experimental

Materials and equipment

Styrofoam or waste-expanded polystyrene (PS) was obtained from plastic waste collected at The University of Edinburgh. 1,2-

Dichloroethane (DCE) and iron(III) chloride (FeCl₃) were purchased from Alfa Aesar. Formaldehyde dimethyl acetal (FDA) and α,α' -dichloro-*p*-xylene (DCX) were purchased from Sigma-Aldrich. Methanol, chloroform, and acetone were purchased from Thermo Fisher Scientific. All chemicals were used as is.

Polytetrafluoroethylene (PTFE) tubes with dimensions of 1/8 in × 0.063 in × 50 ft were purchased from Supelco Inc., while PTFE tube fittings (Y-junction connectors, female union connectors, ferrules, and nuts) were purchased from Nanjing Runze Fluid Control Equipment Co., Ltd. Polypropylene syringes were purchased from MB Fibreglass, while 21G needles were supplied from Becton, Dickinson, and Company. A tube holder was fabricated from polylactic acid (PLA) filaments using a Prusa i3 MK3S 3D printer. The design was based on two different shapes with 7 individual parts, a central ring, and holder wings, which can be hinged on to each other. A peristaltic dosing pump (SEKO Kronos 50) was used to pump the monomer solution as well as cleaning solvents after the operation. A syringe pump (Cole-Parmer® SP210iwz) was deployed to inject the catalyst solution into the reactor.

HCP synthesis in batch reactors

HCPs synthesised in batch reactors were used as control materials here. All batch syntheses were performed in a 250 mL three-neck round-bottom glass flask connected to a reflux condenser. HCPs were synthesised *via*:

(i) Internal crosslinking – 2.884 g of DCX and 2.672 g of FeCl₃ were dissolved in 100 mL DCE. The mixture was heated to 373 K (ref. 24) and continuously stirred with a magnetic stirrer for 24 hours.

(ii) Post-crosslinking – 0.385 g of PS, 0.385 g of FeCl₃, and 0.385 g of DCX were first dissolved in 100 mL of DCE. The mixture was heated to 353 K (ref. 27) *via* an oil bath and continuously stirred with a magnetic stirrer for 24 hours.

(iii) External crosslinking – 0.762 g of PS, 3.810 g of FeCl₃, and 3.810 g of FDA were dissolved in 100 mL of DCE. The mixture was heated to 353 K (ref. 28) *via* an oil bath and continuously stirred with a magnetic stirrer for 24 hours.

HCP synthesis in flow reactors

Fig. 2 and S1† show the experimental set-up of the flow reactor used in this work for HCP synthesis *via* post-, internal, and external crosslinking. The details of the synthesis *via* the flow system are described as follows:

(i) Internal crosslinking – the substrate solution was prepared by dissolving 1.154 g of DCX in 20 mL of DCE. A

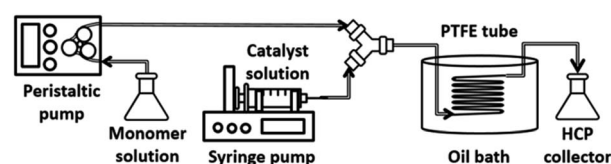


Fig. 2 Schematic showing the equipment used in our flow reactor.



peristaltic pump was used to feed the substrate solution into the system. The catalyst solution was prepared by mixing 1.069 g of FeCl_3 in 20 mL of DCE and then loaded into a syringe and pumped into the system by a syringe pump. All reactants were mixed in a Y-junction connector prior to the entry into the reactor at the total volumetric flow rate of 5.40 mL min^{-1} . The reactor was submerged in a heated oil bath setting at 343 K. The slurry product was collected at the end of the reactor.

(ii) Post-crosslinking – the substrate solution was prepared by dissolving 0.154 g of PS in 20 mL of DCE. The catalyst solution was prepared by mixing 1.524 g of FeCl_3 and 1.524 g of DCX in 20 mL of DCE and then loaded into a syringe. The substrate solution was fed into the system *via* a peristaltic pump, while the catalyst solution was fed *via* a syringe pump. Both solutions were fed into the reactor at the total volumetric flow rate of 2.94 mL min^{-1} and mixed at a Y-junction. The reactor was submerged in a pre-heated oil bath at 343 K. The slurry product was collected at the end of the reactor.

(iii) External crosslinking – the substrate solution was prepared by dissolving 0.305 g of PS in 20 mL of DCE. The catalyst solution was prepared by mixing 1.524 g of FeCl_3 and 1.524 g of FDA in 20 mL of DCE and loaded into a syringe. A peristaltic pump was used for feeding substrate solution into the reactor. A syringe pump was used for feeding the catalyst solution into the system. The total volumetric flow rate was 1.94 mL min^{-1} . Both solutions were mixed at the Y-junction before entering the reactor, which was pre-heated inside the oil bath at 343 K. The slurry product was collected at the end of the reactor.

The reactor volume was approximately 30 mL (1.58 mm inner diameter, 15.21 m length). Our reactor comprised a 50 mm pitch helical coil with multiple curvature radii (34, 39, 44, 49, and 54 mm) designed to minimise the spatial footprint.

Since the reactor volume (V) was fixed, a change in the residence time (τ) depended on the total volumetric feed flow rate (F), as shown in the following equation:

$$F = \frac{V}{\tau}$$

The operating time of flow synthesis (t_{op}) was calculated using the following equation where V_{feed} was denoted as the volume of the feed solution:

$$t_{\text{op}} = \frac{V + V_{\text{feed}}}{F}$$

Upon completion of each synthesis process, either in batch or flow, products were washed with chloroform and methanol until the washings became clear. Then, the samples were soaked overnight in methanol and rewashed in the same way with methanol and acetone. Finally, samples were dried in an oven at 333 K for 8 hours and collected for further characterisation.

Space-time-yield (STY) of HCP synthesis

HCP yield was calculated by dividing the weight of the dried powder produced by the weight of monomers or substrates. The

amount of external crosslinkers was not included in this calculation as the crosslinking could be formed from other halogenated compounds used in synthesis, *i.e.*, the chloro group in DCX (substrate) or DCE (solvent).²⁷ This could lead to a yield value of more than 100%.²⁹ Hence, HCP yield was calculated using the following equation:³⁰

$$\text{Product yield} = \frac{\text{weight of dried particles}}{\text{weight of monomers or substrates}}$$

STY is the term used in flow chemistry to determine how much product, *i.e.*, yield is produced in a reactor volume within a time period. As batch reactions here took place over 24 hours, the operating period for the calculation of the flow system was then fixed to per day unit. The STY calculations for batch and flow systems^{17,31} were shown in the following equations:

$$\text{STY}_{\text{batch}} = \frac{\text{substrate weight per batch} \times \text{product yield}}{\text{volume of solvent per batch}}$$

$$\text{STY}_{\text{flow}} = \frac{\text{inlet substrate weight per day} \times \text{product yield}}{\text{reactor volume}}$$

Characterisation

The pore size distributions of HCPs characterize in this work were characterized with N_2 gas adsorption at 77 K using various gas analysers at The University of Edinburgh, Strathclyde University, and CSIRO, Australia. These isotherms were used to determine the specific surface area and for porosity analysis using the BET theory and density functional theory (DFT) method, respectively, using the AsiQwin software. Rouquerol's four criteria were applied for BET surface area correction for microporous materials (Fig. S4†).^{32,33} Samples were degassed in a vacuum at 373 K for 12 hours before characterisation.

Fourier transform infrared spectroscopy (FTIR) was used to investigate the chemical structure of the reagents and HCPs synthesised in this work. This was achieved with an ATR-FTIR (Nicolet iS10 with Smart iTX Diamond accessory, Thermo Fisher Scientific, Waltham, MA) with 64 scans per sample and a resolution of 0.48 cm^{-1} . The chemical structures of the synthesised HCPs were validated with solid-state ^{13}C cross polarisation (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy using a Bruker Avance III spectrometer with a 9.4 T superconducting magnet.

N_2 and CO_2 adsorption studies at 298 K were performed and the adsorption isotherms were used to calculate CO_2/N_2 selectivity ($S_{\text{CO}_2/\text{N}_2}$) based on the ideal adsorption solution theory (IAST). The standard conditions³⁴ of 298 K and 15 : 85 molar ratio of the inlet gas mixture ($y_{\text{CO}_2} = 0.15$, $y_{\text{N}_2} = 0.85$) were chosen for this calculation using following equations:

$$S_{\text{CO}_2/\text{N}_2} = (x_{\text{CO}_2}/y_{\text{CO}_2})/(x_{\text{N}_2}/y_{\text{N}_2}) = \frac{P_{\text{N}_2}^0}{P_{\text{CO}_2}^0}$$

$$P_i y_i = P_1^0 x_i$$



$$x_{\text{CO}_2} + x_{\text{N}_2} = 1$$

$$y_{\text{CO}_2} + y_{\text{N}_2} = 1$$

$$\int_0^{P_0} \frac{Q_{\text{CO}_2}}{P} dP = \int_0^{P_0} \frac{Q_{\text{N}_2}}{P} dP$$

x_i and y_i denote the mole fraction of gas i (where $i = \text{CO}_2, \text{N}_2$) in the adsorbed phase and gas phase, respectively. P_i^0 is the equilibrium pressure for pure i assuming that spreading pressure (π) was constant during isothermal adsorption. The single-site Langmuir–Freundlich model (SSLF) was selected to associate the adsorbed amount of gas (Q_i) with the function of pressure (P), as shown in the following equation:

$$Q = \frac{qkP^n}{1 + kP^n}$$

The parameters from the SSLF model equation, q , k , and n , represented the maximum-adsorbed amount of pure gas at the adsorption site, the affinity parameter, and the solid heterogeneity respectively. These parameters were obtained from the regression analysis of the experimental adsorption isotherm data.

Transmission electron spectroscopy (TEM) was deployed to characterise HCP morphology. The samples were dispersed in DCE and deposited onto carbon-coated copper grids (Agar Scientific). Excess solvent was blotted away and the grid was air-dried. Samples were imaged in an FEI F20 microscope operating at 200 kV. The images were taken under low-dose conditions using a Gatan Rio CCD camera. The micrographs (Fig. S8) are shown in ESI.†

Results and discussions

The productivity of the flow processes

Here, we show that HCP synthesis duration could be reduced, from 24 hours to 5–15 minutes in a flow reactor *via* internal-, post-, and external crosslinking strategies (Table 1). This was attributed to the enhanced heat and mass transfer rates associated with the higher specific area (the ratio of the surface area to volume)³⁵ of the flow reactor deployed in this work. The specific area of the flow reactor deployed in this work was 5087 m² m^{−3}, 68 fold higher than the 75 m² m^{−3} of the batch reactor used here (Table S4†). Reactors with a high surface area to volume ratio³⁵ typically possess the advantages of rapid heat and mass transfers that enhance the reaction kinetics.³⁶

In our work, heat transfer was mainly impacted by this significant difference in reactor-specific surface area. The larger specific surface area of the flow reactor enhanced heat transfer, *i.e.*, the energy flow from the oil bath to the reactor walls that were in close contact with the reactants inside the reactor. At the same time, the small volume of the flow reactor offered short diffusion pathways (better mass transfer) to enable faster mixing.³⁷ The combination of these factors was favourable for polymerisation/crosslinking kinetics. The effects of the thermal conductivity of the reactor material and heat source temperature were negligible here. The difference in thermal conductivities between the glass batch reactor (1 W m^{−1} K^{−1})³⁸ and polytetrafluoroethylene (PTFE) flow reactor (0.25 W m^{−1} K^{−1})³⁹ was 4 times, while the difference in heat source temperatures used in both batch and flow syntheses was only 10 K.

In terms of mass transfer, a higher degree of mixing is favourable for the reaction as reagent particles have more access to the reactor surface where the highest heat energy is provided.¹⁷ The mixing efficiency could be correlated to the

Table 1 Operating parameters of HCP synthesis in batch and flow systems and their corresponding yield

Crosslinking approach	Substrate–crosslinker type	Substrate concentration [% w/v]	Substrate : FeCl ₃ : crosslinker	Temperature [K]	Volumetric flow rate [mL min ^{−1}]	Reaction time ^a [min]	HCP yield [%]	Sample ^b
Internal crosslinking	DCX–N.A.	2.884	1 : 1 : 0 (mol)	373	N.A.	1440	58.50	I-B-HCP
		2.884	1 : 1 : 0 (mol)	343	5.40	5	7.24	I-F-HCP
Post-crosslinking	PS–DCX	0.385	1 : 1 : 1 (wt)	353	N.A.	1440	155.38	P-B-HCP
		0.385	1 : 1 : 1 (wt)	343	2.94	10	126.72	P-F-HCP
External crosslinking	PS–FDA	0.762	1 : 5 : 5 (wt)	353	N.A.	1440	156.63	E-B-HCP
		0.762	1 : 5 : 5 (wt)	343	1.94	15	114.30	E-F-HCP

^a Residence time is an equivalent term for reaction time in the flow system. ^b The samples were named X-Y-HCP in which X denotes hypercrosslinking approach (I for internal crosslinking, P for post crosslinking, E for external crosslinking) and Y denotes synthesis system (B for batch reactions, F for flow synthesis).



dimensionless Reynolds number (Re) which describes fluid flow patterns – laminar, transient, and turbulence. Turbulent flow is typically associated with good mixing as an external driving force is applied to induce particle diffusion, rather than relying solely on molecular diffusion.¹⁷ In a stirred tank reactor, the turbulent region is where $Re > 10\,000$,⁴⁰ while turbulent fluid flow in a helical coil reactor is where $Re > 40$.⁴¹

Using an equation for a propeller turbine mixer tank,⁴² we estimated that the Re number in our batch reactor reached a value of 6524 (see ESI†). This indicated transient fluid flow (the transition region between laminar and turbulent flow pattern, $100 < Re < 10\,000$) in our batch reactor, *i.e.*, moderate mixing efficiency. Meanwhile, the Re number in our coil flow reactor (Table S5†) during the synthesis of E-F-HCP (15 minutes residence time) was estimated to be 65. This indicated turbulent mixing in our flow reactor. Clearly, the coiled reactor used in this work provided better mixing rates, enhancing polymerisation/crosslinking kinetics.²⁰

The advantage of short reaction times in flow synthesis resulted in an increase in STY (Fig. 3). With flow synthesis, the STY value improved by 32 fold for internal crosslinking, 117 fold for post-crosslinking, and 68 fold for external crosslinking. This addressed the issue of low HCP productivity rates due to time constraints required in batch reactions that we have now overcome with flow synthesis.

Chemical structures of flow-produced HCPs

The chemical structures of these HCPs were characterised and validated with FTIR and ¹³C-NMR analyses. HCPs synthesised in batch reactors were used as control materials. The nomenclature for HCPs synthesised in this work is summarised in Table 1, alongside the type of reagents and operating conditions.

Comparing the FTIR spectra of HCPs synthesised by internal crosslinking in batch (I-B-HCP) and continuous flow (I-F-HCP) reactions, we observed that in both samples, the infrared peak intensities correlated to C–Cl vibrations^{27,43,44} at 668 and 1260 cm^{-1} and C–H bending⁴⁴ at 854 cm^{-1} were reduced when compared to the unreacted DCX precursor (Fig. 4a). This was ascribed to chloromethyl substitution at the *para* position, suggesting that the chloro group was eliminated during Friedel–Crafts alkylation. The intensities of peaks correlated to the skeletal benzene rings, such as aromatic C–H stretching⁴³ at 2971 and 2866 cm^{-1} and aromatic C=C stretching^{43,45} at 1421, 1445, and 1512 cm^{-1} were also reduced. This suggested the

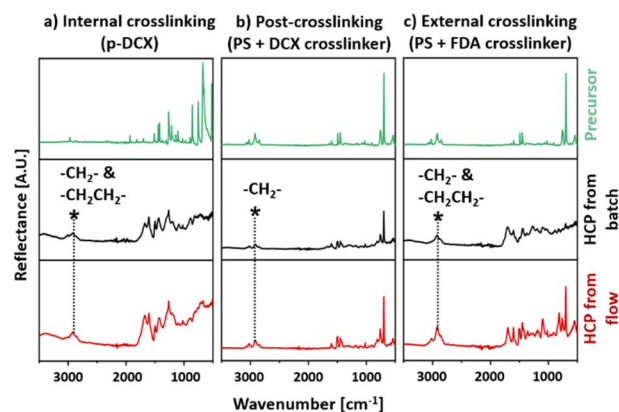


Fig. 4 FTIR spectra of the HCPs and their precursors: (a) internal crosslinking (p-DCX), (b) post-crosslinking (PS + DCX crosslinker), (c) external crosslinking (PS + FDA crosslinker).

success of DCX crosslinking.⁴⁵ At the same time, the peak corresponding to C–H stretching⁴⁵ at 2923 cm^{-1} from HCP broadened when compared to that of DCX. This was due to the overlapping original C–H stretching peak with the newly formed methylene bridge ($-\text{CH}_2\text{CH}_2-$) crosslinks.⁴⁵ This type of cross-linked bridge was formed from DCE molecules that functioned as both a solvent and a crosslinker reagent.⁴⁶

The FTIR spectra of HCPs synthesised *via* post-crosslinking, P-B-HCP, and P-F-HCP (Fig. 4b), resembled that of PS. We observed peaks that corresponded to aromatic C–H stretching at 3087, 3061, 3027 cm^{-1} , C–H bending at 756, 696 cm^{-1} , aromatic C=C stretching at 1603, 1493, 1453 cm^{-1} , C–H bending at 854 cm^{-1} and backbone C–H stretching at 2921 and 2849 cm^{-1} .²⁸ However, these peaks were less intense than those of PS. These indicated that the aromatic benzene rings of PS were modified during post-crosslinking. These trends were also presented in the FTIR spectra of HCPs synthesised *via* external crosslinking, E-B-HCP, and E-F-HCP (Fig. 4c). The broadened peak corresponding to C–H stretching⁴⁵ centred at 2921 cm^{-1} similar to the spectra of internally crosslinked HCPs was observed in these spectra. This indicated that $-\text{CH}_2\text{CH}_2-$ crosslinks were also formed in the externally crosslinked HCP. The presence of newly formed crosslinking methylene bridges in these HCPs was also validated with ¹³C-NMR.

The ¹³C-NMR spectra of I-B-HCP and I-F-HCP (Fig. 5a) contained major peaks centred at 138, 35, and 16 ppm. These peaks were correlated to the substituted aromatic carbon,⁴⁷ the crosslinked bridges from *via* FDA^{28,47} and DCE,²⁷ respectively. There were also unreacted DCX^{24,48} in these samples as we also observed peaks centred at 43 ppm (carbon in $-\text{CH}_2\text{Cl}$) and 128 ppm (non-substituted aromatic ring). The spectra of P-B-HCP and P-F-HCP (Fig. 5b) also contained a peak centred at 146 ppm correlated to the quaternary non-substituted aromatic carbon^{48,49} from the parent PS molecule. These spectra also contained peaks at 136 and 128 ppm, which corresponded to substituted aromatic carbon and non-substituted aromatic rings from both PS and DCX,

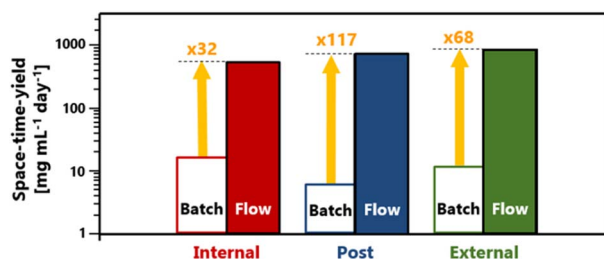


Fig. 3 STY of HCP from batch and flow production.



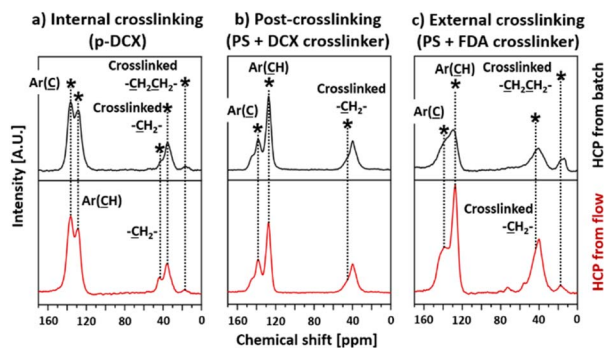


Fig. 5 ^{13}C -NMR spectra of the HCPs: (a) internal crosslinking (p-DCX), (b) post-crosslinking (PS + DCX crosslinker), (c) external crosslinking (PS + FDA crosslinker).

respectively. The broad peak centred at 40 ppm in these spectra was a mixture of signals attributed to aliphatic methylene carbon, methine backbone carbon, and methylene crosslink bridges.⁴⁸ We did not observe any peaks corresponding to chloromethyl carbon in these samples. The ^{13}C -NMR spectra of E-B-HCP and E-F-HCP (Fig. 5c) were like those of HCPs produced from post-crosslinking.

HCP microporosity

Porosity in HCPs is formed as a function of the crosslinking degree.⁵⁰ As the degree of crosslinking increases, the BET surface area increases, resulting from the creation of micropores (<2 nm).^{46,50} However, as the micropores are excessively developed within the HCPs, this then results in the decline of BET surface area when a certain degree of crosslinking is achieved.¹ Here we observed that the BET surface areas of the flow-produced HCPs were in the range between 800–1160 $\text{m}^2 \text{g}^{-1}$ similar to reported batch-produced HCP counterparts from literature.^{24,27,28} Regardless of crosslinking strategies, the BET surface areas were lower than those of HCPs synthesised in batch reactors by 1.5–9.6%, while the total pore volume of flow-produced HCPs was on average 21% lower (Table 2). However, the enhancement of micropore volume in the flow-

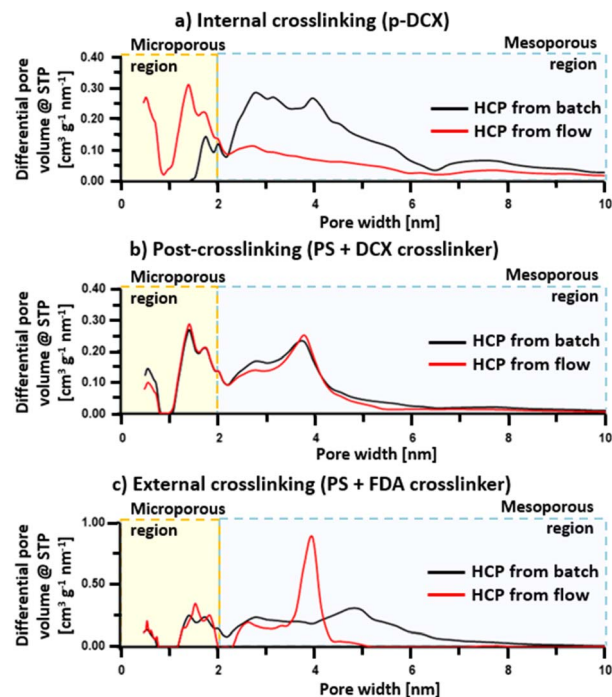


Fig. 6 Pore size distribution of flow-produced HCPs and their batch equivalents.

produced HCPs synthesised *via* internal and external crosslinking leads to the formation of narrower pores between 0–10 nm (Fig. 6). These results indicate that flow synthesis created more microporosity in such HCPs. This difference in micropore volume between HCP synthesised from batch and flow reactions could be attributed to different heat-mass transfer rates of reactor types, leading to different crosslinking rates and intensities. For batch synthesis, we used a 250 mL three-neck round-bottom glass flask as a reactor. Meanwhile, for flow synthesis, we used a 30 mL PTFE helical coil tube as a reactor. The smaller volume of the coiled tube induced faster mixing of reactants,³⁶ and enhanced mass transfer³⁵ when compared to the glass flask. The helical coil also increased the vortex flow pattern inside the tube.⁴¹ Moreover, the contact area for transferring heat energy from the oil bath to the reaction mixture is larger in the flow reactor. The increment in microporosity in flow-produced HCP could potentially benefit applications, such as gas separation and storage.

The existence of micropores was confirmed through the steep slope at lower relative pressure, where $P/P_0 < 0.05$ (Fig. S5†). Based on IUPAC classification,⁵¹ the isotherms of internally crosslinked HCPs were a mixture of type I and IV. Moreover, the presence of macropores (>50 nm) in the internally crosslinked HCPs could be observed in the isotherm at $P/P_0 > 0.9$. It should be noted that this was the only HCP type in this study that formed macropores. The isotherms of HCPs synthesised by post-crosslinking and external crosslinking were classified as type IV, where ink bottle-like pore shapes were more prevalent. The hysteresis loops of these HCPs indicated

Table 2 Textural properties of each HCP sample^a

Samples	BET surface area [$\text{m}^2 \text{g}^{-1}$]	DFT total pore volume [$\text{cm}^3 \text{g}^{-1}$]	DFT micropore volume [$\text{cm}^3 \text{g}^{-1}$]
I-B-HCP	964	1.263	0.042
I-F-HCP	950 (−1.5%)	1.014 (−19.7%)	0.281 (+569%)
P-B-HCP	903	0.788	0.203
P-F-HCP	816 (−9.6%)	0.650 (−17.3%)	0.195 (−3.9%)
E-B-HCP	1162	1.219	0.184
E-F-HCP	1092 (−6.0%)	0.917 (−24.8%)	0.293 (+59.2%)

^a DFT micropore volume data were obtained from the cumulative pore volume of the pore size up to 2 nm.



that there were significant amounts of small mesopores (2–10 nm) within these HCPs, which correlated to the broad peaks in the pore size distributions (Fig. 6).

The microporosity of HCPs studied here could be tailored by varying synthesis parameters: residence time, feed solution composition and concentration, and temperature. Here we observed that at a fixed substrate concentration, reagent ratios, and temperatures, an increase in residence time from 10 to 15 minutes typically enhanced the micropore volume of externally crosslinked HCPs by 595%. However, a further increase of residence time to 20 minutes reduced micropore volume by 65.5% (Table S3†). Similar trends were observed in batch reactions over 12 and 24 hour periods.¹ Prolonged reaction times could lead to excessive crosslinking, forming pores that are smaller than the kinetic diameter of N₂, the gas used to probe porosity content during gas adsorption experiments. Another reason for an optimised micropore volume in HCPs produced *via* 15 minutes of residence time in flow reactors could be the mixing intensity. Our calculation (Table S5†) showed that with a residence time of 15 minutes, the Reynolds number of our reactor reached a value of 65. This was closest to the optimal Reynolds number of 40 in helical reactors.⁴¹ Here it is important to highlight that the optimisation of HCP porosity by tailoring residence time did not drastically affect STY, *i.e.*, productivity rate. The highest STY value of 965 mg mL⁻¹ day⁻¹ was achieved with a residence time of 10 minutes. The increase of residence time to 15 minutes reduced this STY value by 28.3%, reaching 692 mg mL⁻¹ day⁻¹.

The enhancements in both micropore volume and STY were observed (Table S3†) when the weight ratio of PS by FeCl₃ by FDA increased from 1 : 1 : 1 to 1 : 5 : 5 while fixing the other three synthesis parameters. No solid was formed at the weight ratio of 1 : 1 : 1. This indicates that crosslinking did not occur. Although a similar test in the batch system showed that the crosslinking using a 1 : 1 : 1 ratio of PS to FeCl₃ to FDA is achievable,²⁸ shorter residence time and lower temperature in flow reactors might be insufficient to induce crosslinking when there is a low ratio of catalyst and crosslinker to the substrate. HCP products were obtained when the weight ratio was increased to 1 : 3 : 3, with a STY of 981 mg mL⁻¹ day⁻¹. However, the micropore volume of 0.006543 cm³ g⁻¹ was the lowest among all the externally crosslinked HCPs. The increase in micropore volume and the STY when increasing the ratio from 1 : 3 : 3 to 1 : 5 : 5 was 1493% and 47.5%, respectively. Similar trends showing the improvement of the specific surface area, as a result of pore generation, and product yield were also observed in batch HCP synthesis.^{24,28} The higher amount of the catalyst and crosslinker in the system indicated a higher possibility of the substrate getting involved in the reaction. Hence, the suitable weight ratio of substrate to the catalyst to crosslinker for flow synthesis in our system was 1 : 5 : 5.

Increasing the reaction temperature while fixing the residence time, substrate concentration, and chemical ratio did not enhance STY (average of 830 mg mL⁻¹ day⁻¹), however, micropore volumes were enhanced. The increase in the temperature from 333 to 343 K increased the micropore volume by 84.8% from 0.059 to 0.109 cm³ g⁻¹. This indicated that

elevating temperature by a 10 K difference in our system affected the crosslinking degree in HCPs.

The impact of PS concentration on micropore volume was subtle compared with the other three synthetic parameters. The amount of micropore volume was increased by just 37.5% from 0.4% to 0.6% w/v of PS. Increasing the substrate concentration from 0.6 to 0.8% w/v and then to 1.0% w/v slightly increased and decreased micropore volume by 5.7% and 9.5%, respectively. This trend was also observed in batch synthesis,^{24,46} which suggested that the fabrication of microporous polymers, *i.e.*, HCP is not sensitive to the monomer concentration as much as macroporous polymers.²⁴ On the other hand, the substrate concentration caused the largest influence on STY among all four synthetic parameters, as the correlation between PS concentration and STY was directly proportional. Increasing the PS concentration from 0.4% to 1.0% w/v enhanced STY by 3 fold from 457 to 1447 mg mL⁻¹ day⁻¹.

With these optimal synthesis parameters, we were able to enhance the STY of HCP synthesis using flow reactions, as shown earlier in Fig. 3. This inferred that we were able to not only enhance the microporosity of the internally crosslinked HCPs but also improve the STY of such HCPs.

CO₂/N₂ separation

Due to higher total pore volumes in batch-produced HCPs (Table 2), the CO₂ and N₂ uptakes (Fig. 7) of such HCPs, regardless of crosslinking strategies, were higher than those synthesised under a continuous flow. Amongst all the HCPs studied here, the total pore volume of HCPs synthesised *via* internal crosslinking in batch reactions were the highest, reaching 1.26 cm³ g⁻¹. As such, the CO₂ and N₂ uptakes of HCPs synthesised *via* internal crosslinking reached 0.99 and

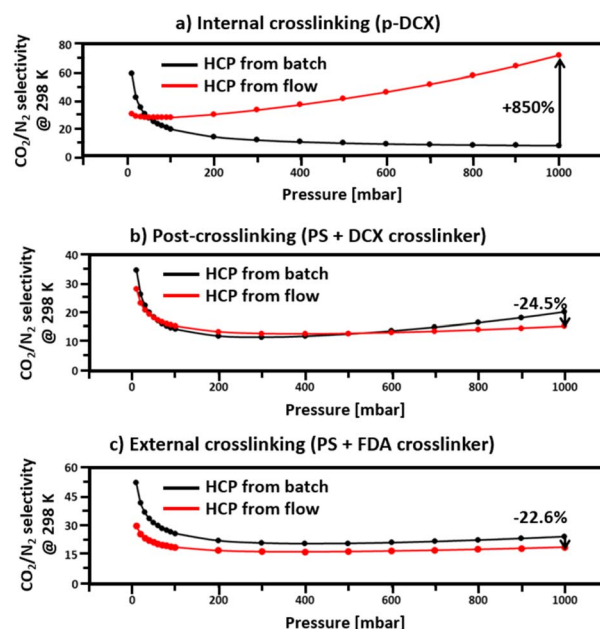


Fig. 7 CO₂/N₂ selectivity at 298 K, 1 atm, 15 : 85 of CO₂ : N₂ inlet gas mixture.



0.27 mmol g⁻¹, respectively. With a total pore volume of 1.22 cm³ g⁻¹, the CO₂ and N₂ uptakes of HCPs synthesised in batch reactions *via* external crosslinking reached 0.8 and 0.1 mmol g⁻¹, respectively. These were 19% and 63% lower than those of I-B-HCP. With the lowest total pore volume of 0.79 cm³ g⁻¹, HCPs synthesised through post-crosslinking in batch reactions only uptake 0.55 and 0.05 mmol g⁻¹ of CO₂ and N₂, respectively. Although continuous flow synthesis reduced the total pore volume of HCPs by 17–25% (Table 2), leading to lower CO₂ and N₂ uptakes, this approach enhanced the micropore volumes in internally and externally crosslinked HCPs by 569% and 59%, respectively. The 569% increase in the micropore volume in internally crosslinked HCPs underpinned a CO₂/N₂ selectivity (at 298 K and 1000 mbar) of 71.5, 850% higher than that of batch-produced internally crosslinked HCPs, which was the lowest amongst all samples studied here, at 7.5 (Fig. 7). This significant difference in CO₂/N₂ selectivity between the flow and the batch produced internally crosslinked HCPs could be attributed to the amount and type of pores present. With 25% more total pore volume, more CO₂ and N₂ could be adsorbed in I-B-HCPs. However, with only 3.2% of micropores, the ability to separate CO₂ from N₂ in I-B-HCPs is diminished. Due to the similar kinetic diameters of N₂ (3.64 Å) and CO₂ (3.30 Å),⁵² materials with small pore sizes and narrow pore size distributions are required for effective CO₂/N₂ separations, especially for post-carbon capture⁵³ and ideally, the pore sizes should be between 5 to 7.8 Å.⁵³ In this work, such pores were only observed in HCPs synthesised in flow reactions *via* internal crosslinking. Hence, the CO₂/N₂ selectivity (calculated using IAST theory with 0.15 bar CO₂ partial pressure, 298 K and 1 atm) of these HCPs were the highest amongst all HCPs studied here. This outcome demonstrated that HCP CO₂/N₂ selectivity could be improved through optimisation of the reaction parameters *via* reactor design, *i.e.*, from batch to flow reactor type. This is unique from existing strategies such as HCP functionalisation,^{21–23} the use of bespoke monomers^{25,26} and tailoring synthesis conditions (heat, duration, *etc.*).

Conclusions

This study highlights two key benefits of the implementation of continuous flow synthesis in HCP production. First, we observed higher microporosity in HCPs synthesised in flow reactors. Regardless of their lower total pore volumes and BET surface areas, high volumes of micropores within flow-produced HCPs enhanced CO₂/N₂, reaching a value of 71.5. We also verified that the porosity can be tailored through the alteration of flow synthetic parameters. When comparing our optimised internally crosslinked HCPs with their batch counterpart, the HCP from flow synthesis showed an increase in micropore volume by 569% resulting in an 850% increase in CO₂/N₂ separation. Second, the optimal residence time was reduced to 5 minutes with flow synthesis, instead of 24 hours as in a batch operation. This enhanced the productivity of STY by 32 fold, which resulted in a HCP production rate of 563 mg cm⁻³ day⁻¹. We also demonstrated the versatility of flow reactions for HCP synthesis *via* post-crosslinking and external

crosslinking approaches. The findings from this work show the potential to scale up HCP synthesis with flow reactors to meet the global demand for such materials, and the potential for carbon capture. The pilot scale of this process should be the next step, focusing on the optimisation of operating parameters.

Author contributions

The study was proposed by C. H. L. The conceptualised idea was discussed between N. C. and C. H. L. The synthesis process was conducted by N. C. The contribution of N₂ gas analysis characterisation was shared between L. D. and A. J. F. FTIR characterisation was conducted by S. L. and S. S. ¹³C-NMR characterisation was done by D. M. D. CO₂ and N₂ adsorption tests for CO₂/N₂ separation were performed by K. K., and M. R. H. All the results were analysed by N. C. The paper was prepared by N. C. with supervision from C. H. L.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

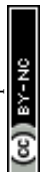
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Support Information

Flow synthesis of hypercrosslinked polymers with additional microporosity that enhance CO₂/N₂ separations

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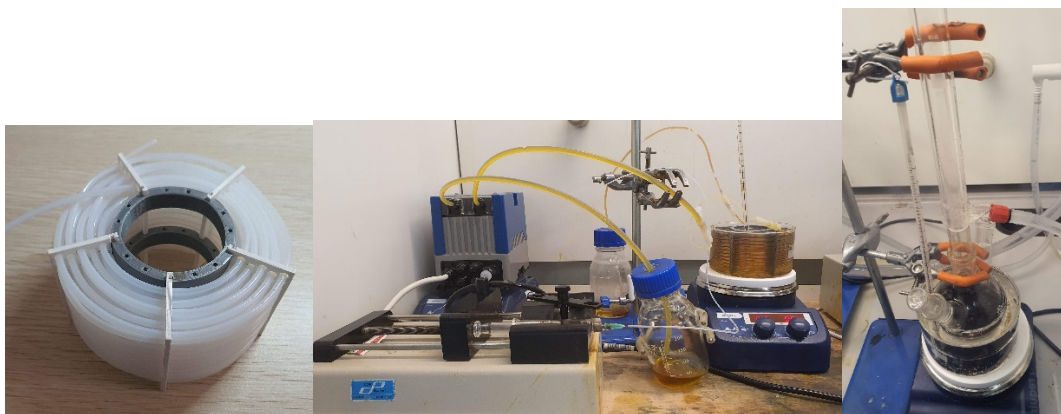


Figure S1 Coiled tubular reactor (Left), continuous flow set-up (Centre), and batch set-up (Right)

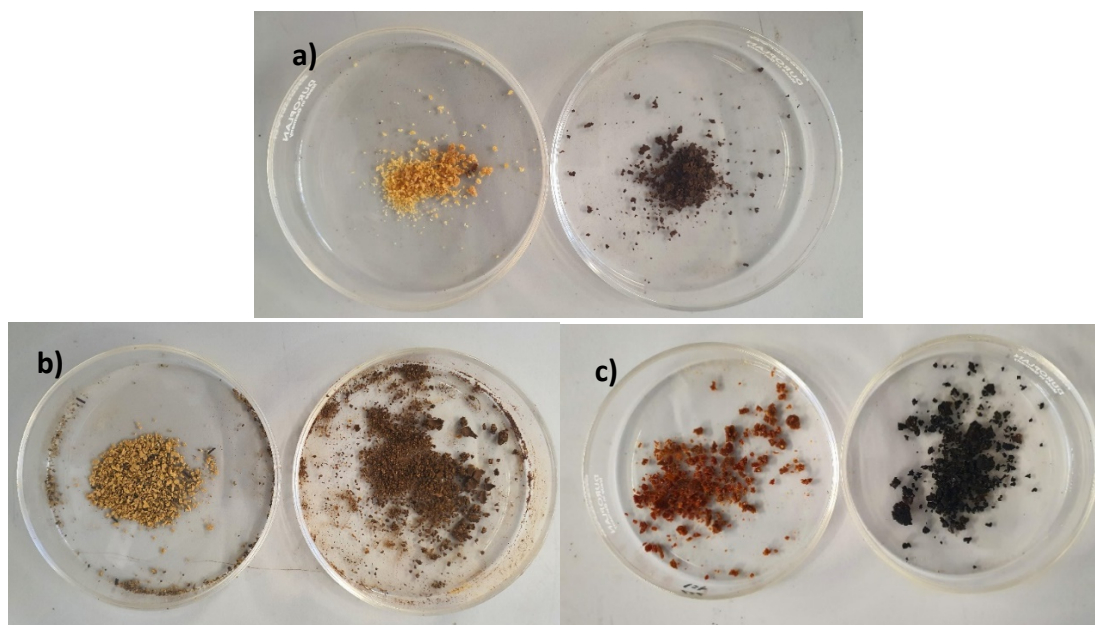


Figure S2 HCPs from the optimal flow-condition (Left) with their batch counterpart (Right): a) p-PS/DCX, b) p-DCX, and c) p-PS/FDA

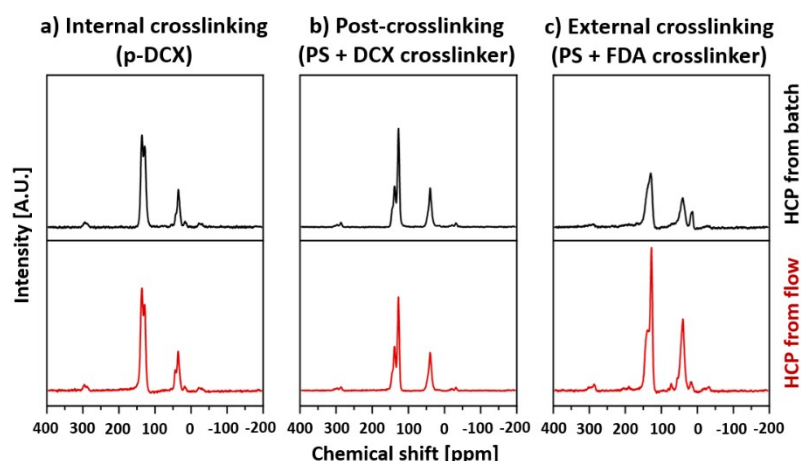


Figure S3 ^{13}C -NMR spectra (Full range from -200 to 400 ppm) of the HCPs

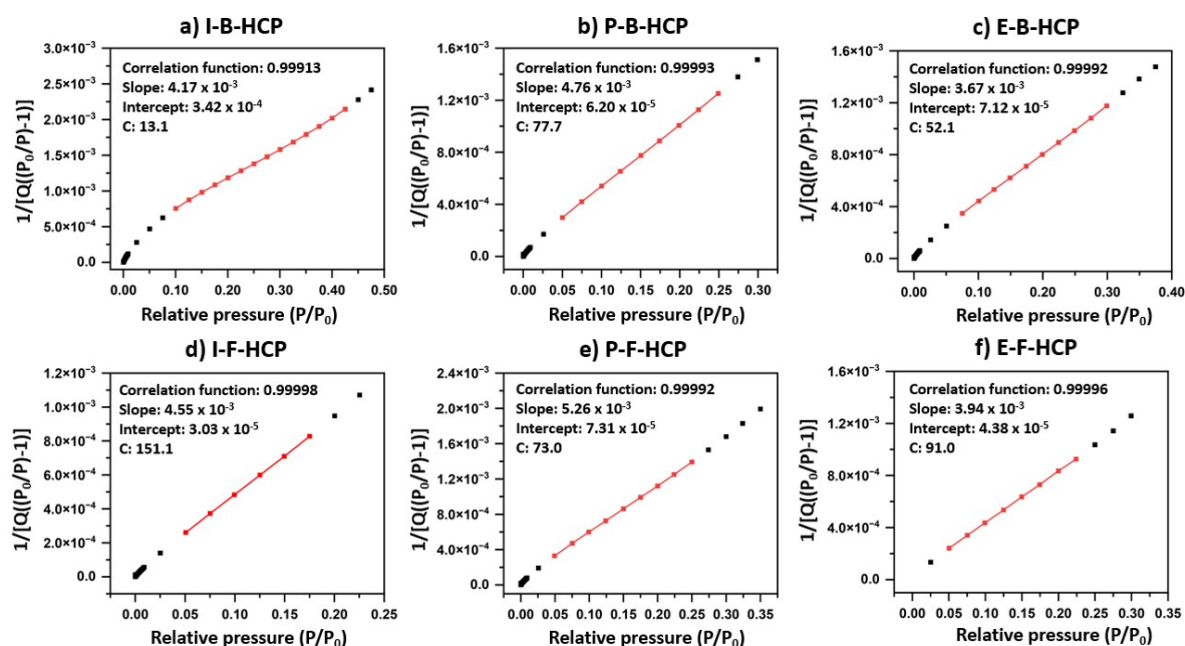


Figure S4 BET plots of six optimal HCP samples of each synthetic approaches (Internal crosslinking, post-crosslinking, and external crosslinking) and synthetic methods (Batch and flow). The fitting region following Rouquerol correction for microporous materials is shown in red dot and line together with correlation function, slope, intercept, and BET constant.

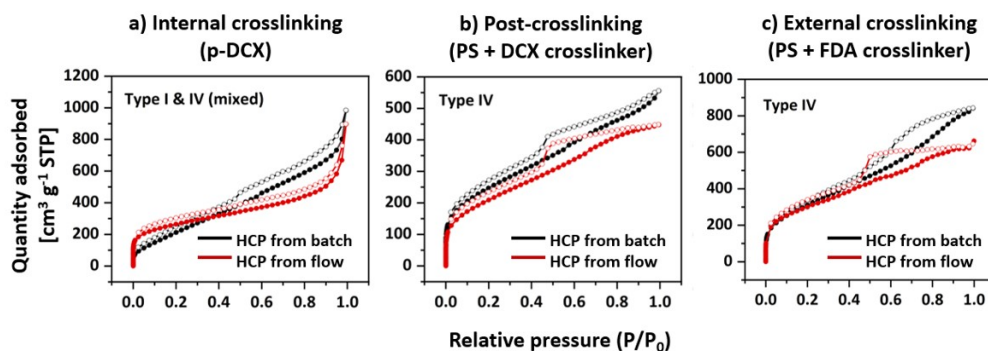


Figure S5 N_2 sorption at 77 K of HCP products. Adsorption isotherm is shown as filled dot marker. Desorption isotherm is shown as empty dot marker.

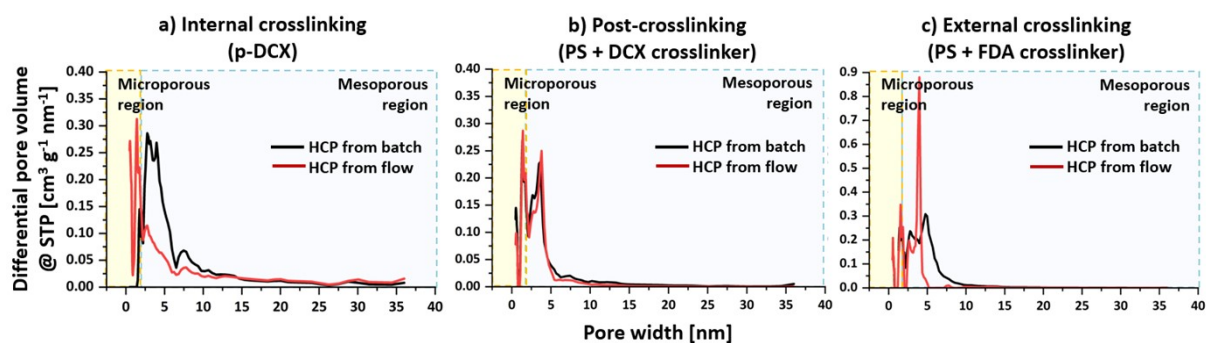


Figure S6 Pore size distribution from 0 – 40 nm pore width of flow-produced HCPs and their batch equivalents

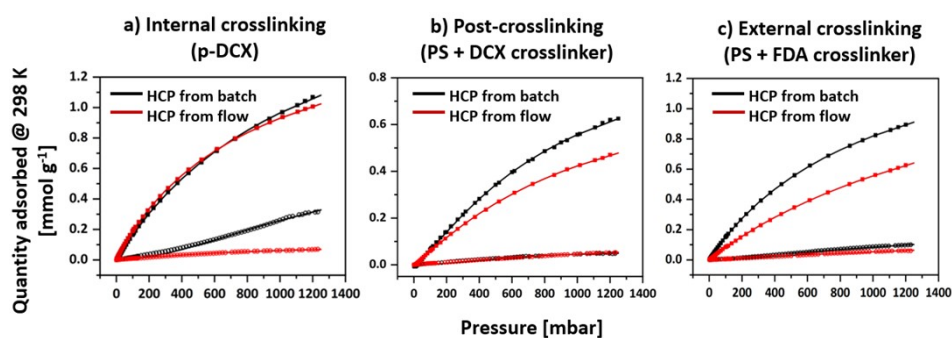


Figure S7 CO₂ uptake isotherms at 298 K. Experimental data is presented as marker points. IAST curve fitting is shown as solid lines. CO₂ adsorption is shown as filled square marker. N₂ adsorption is shown as empty circle marker.

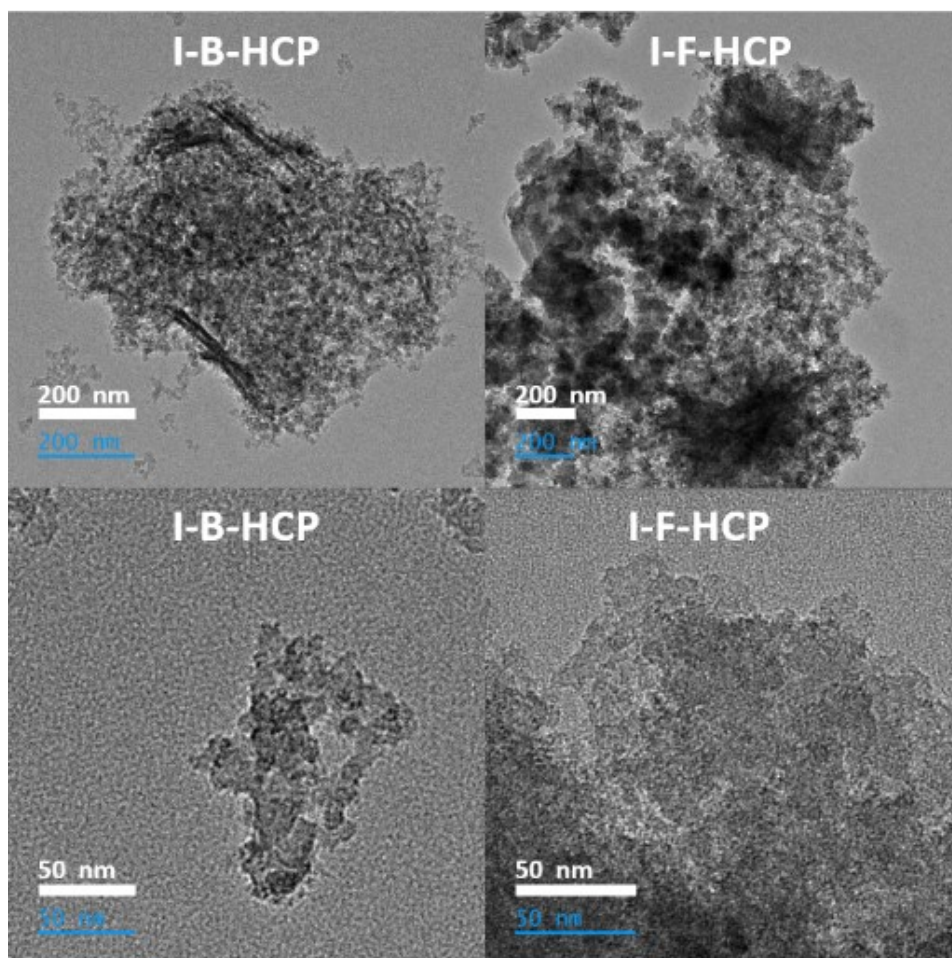


Figure S8 TEM images of I-B-HCP and I-F-HCP

Table S1 Operating parameters of batch production and correspond product yields

Crosslinking approach	Substrate conc. [% w/v]	Substrate: FeCl ₃ : Crosslinker	Temp. [K] ²⁴	Reaction time [day] ⁴¹	Yield [%]	BET SA [m ² g ⁻¹]	Sample names
Internal crosslinking	1.923	1:1:0 (mol)	373	24	64.42	686.356	-
	2.884	1:1:0 (mol)	373	24	58.50	964.309	I-B-HCP
Post-crosslinking	0.385	1:1:1 (wt)	353	24	155.38	903.183	P-B-HCP
External crosslinking	0.762	1:5:5 (wt)	353	24	156.63	1161.864	E-B-HCP

Table S2 Operating parameters of flow production and correspond product yields

Internal crosslinking approach							
DCX conc. [% w/v]	DCX:FeCl ₃ (molar ratio)	Temp. [K]	Flow rate [mL min ⁻¹]	Residence time [min]	Yield [%]	BET SA [m ² g ⁻¹]	Sample names
0.962	1:1	343	1.94	15	Unreacted	N.A.	-
0.962	1:1	343	1.46	20	3.59	N.A.	-
1.923	1:1	343	2.94	10	Unreacted	N.A.	-
1.923	1:1	343	2.26	13	12.19	542.197	-
1.923	1:1	343	1.94	15	Clogged	N.A.	-
2.884	1:1	343	9.40	3	Unreacted	N.A.	-
2.884	1:1	343	5.40	5	7.24	950.130	I-F-HCP
2.884	1:1	343	4.14	7	Clogged	N.A.	-
0.673	1:2	343	9.40	3	17.83	702.780	-
Post-crosslinking approach							
PS conc. [%w/v]	PS:FeCl ₃ : DCX (weight ratio)	Temp. [K]	Flow rate [mL min ⁻¹]	Residence time [min]	Yield [%]	BET SA [m ² g ⁻¹]	Sample names

0.385	1:1:1	343	4.14	7	Unreacted	N.A.	-
0.385	1:1:1	343	2.94	10	126.72	815.900	P-F-HCP
0.385	1:1:1	343	2.26	13	133.51	771.330	-
0.385	1:1:1	343	1.94	15	Clogged	N.A.	-
0.577	1:1:1	343	9.40	3	Clogged	N.A.	-
0.385	1:2:2	343	9.40	3	119.15	N.A.	-
0.385	1:2:2	343	5.40	5	Clogged	N.A.	-

External crosslinking approach							
PS conc. [%w/v]	PS:FeCl ₃ :		Flow rate [mL min ⁻¹]	Residence time [min]	Yield [%]	BET SA [m ² g ⁻¹]	Sample names
	FDA (weight ratio)	Temp. [K]					
0.762	1:5:5	343	2.94	10	85.30	711.388	-
0.762	1:5:5	343	2.26	13	103.70	893.733	-
0.762	1:5:5	343	1.94	15	114.30	1091.656	E-F-HCP
0.762	1:5:5	343	1.74	17	98.01	647.282	-
0.762	1:5:5	343	1.46	20	94.51	377.181	-
0.962	1:1:1	343	2.94	10	Unreacted	N.A.	-
0.962	1:3:3	343	2.94	10	69.48	28.542	-
0.962	1:5:5	343	2.94	10	102.47	534.331	-
0.577	1:5:5	323	2.94	10	Unreacted	N.A.	-
0.577	1:5:5	333	2.94	10	97.65	214.311	-
0.577	1:5:5	343	2.94	10	99.17	671.391	-
0.385	1:5:5	343	2.94	10	80.65	296.193	-
0.577	1:5:5	343	2.94	10	99.17	671.391	-
0.762	1:5:5	343	2.94	10	110.74	605.777	-
0.962	1:5:5	343	2.94	10	102.47	534.331	-

Table S3 Micropore volumes, and STY of flow-produced external crosslinked HCPs from different synthesis parameters

Residence time [min]	DFT micropore volume [cm ³ g ⁻¹]	Space-time-yield [mg mL ⁻¹ day ⁻¹]
10	0.042150	964.514
13	0.083919	897.427
15	0.292950	691.573
17	0.198340	652.577
20	0.101110	526.243

PS:FeCl ₃ :FDA (weight ratio)	DFT micropore volume [cm ³ g ⁻¹]	Space-time-yield [mg mL ⁻¹ day ⁻¹]
1:1:1	N.A.	N.A.
1:3:3	0.006543	981.166
1:5:5	0.104223	1447.037

Temperature [K]	DFT micropore volume [cm ³ g ⁻¹]	Space-time-yield [mg mL ⁻¹ day ⁻¹]
323	N.A.	N.A.
333	0.058939	828.693
343	0.108909	841.592

PS concentration [% w/v]	DFT micropore volume [cm ³ g ⁻¹]	Space-time-yield [mg mL ⁻¹ day ⁻¹]
0.40	0.079204	457.185
0.60	0.108909	841.592
0.80	0.115116	1252.172
1.00	0.104223	1447.037

* DFT micropore volume data was obtained from the cumulative pore volume of the pore size up to 2 nm

Table S4 Surface area, volume, and specific area of batch and flow reactors

Reactor types	Reactor surface area [m ²]	Reactor volume [m ³]	Reactor specific areas [m ² m ⁻³]
Batch: 250mL three neck round bottle *	0.0101	1.340 x 10 ⁻⁴	75
Flow: Helical coil reactor	0.1520	2.988 x 10 ⁻⁵	5087

* Assumed the sphere shape bottle of 8 cm diameter is half filled

Table S5 Reynolds numbers from the synthesis of externally crosslinked HCPs in flow reactor at different residence times

Residence time [min]	Volumetric flow rate [mL min ⁻¹]	Feed flow velocity [m s ⁻¹]	Reynolds number*
10	2.94	0.02499	98.14
13	2.26	0.01921	75.44
15	1.94	0.01649	64.76
17	1.74	0.01479	58.08
20	1.46	0.01241	48.73

$Re = \frac{\rho V D}{\mu} = \frac{\rho F D}{\mu A_{cross}}$ where ρ [kg m⁻³] is fluid density; V [m s⁻¹] is fluid velocity; D [mm] is tube inner diameter; μ [mPa · s] is fluid dynamic viscosity; F [mL min⁻¹] is fluid volumetric flow rate; and A_{cross} [mm²] is cross-sectional area of the tube

** DCE thermodynamic properties at 343 K are $\mu = 0.476 \text{ mPa} \cdot \text{s}$ and $\rho = 1183 \text{ kg m}^{-3}$

*** $D = 1.58 \text{ mm}$, thus $A_{\text{cross}} = 1.96 \text{ mm}^2$

Table S6 Single site Langmuir-Freundlich parameters of HCPs for CO₂/N₂ selectivity calculation

Samples	CO ₂				N ₂			
	q	k	n	R^2	q	k	n	R^2
I-B-HCP	2.08438	8.45×10^{-4}	1.00271	0.99984	0.69661	1.69×10^{-6}	1.84764	0.99632
I-F-HCP	1.78092	1.44×10^{-3}	0.96006	0.99999	0.13976	5.43×10^{-4}	1.05481	0.99868
P-B-HCP	1.00444	1.99×10^{-4}	1.26554	0.99906	0.05773	2.72×10^{-6}	2.03761	0.98983
P-F-HCP	0.87939	4.03×10^{-4}	1.12066	0.99984	0.09412	2.50×10^{-5}	1.52846	0.99668
E-B-HCP	1.68105	1.07×10^{-3}	0.98250	0.99999	0.20433	3.33×10^{-5}	1.44437	0.99944
E-F-HCP	1.70057	5.57×10^{-4}	0.98019	0.99997	0.15265	9.61×10^{-5}	1.24803	0.99895

Estimation of Reynolds number in batch reactor

The Reynolds number in our batch reactor (250 mL three neck round bottom flask) was estimated using an equation for a propeller turbine mixer tank⁴² in which the propeller is equivalent to the stirrer bar in our work. The thermodynamic properties of feed fluid mixture were assumed as pure DCE at 343 K since the concentration of feed was considerably low. The equation is shown as follows:

$$Re = ND^2 \frac{\rho}{\mu}$$

N [rps] is rotational speed of the stirrer bar, which was set to 250 rpm or 4.167 rps

D [m] is diameter of the stirrer bar, which was 0.025 m

μ [mPa · s] is fluid dynamic viscosity, which is 0.476 mPa s

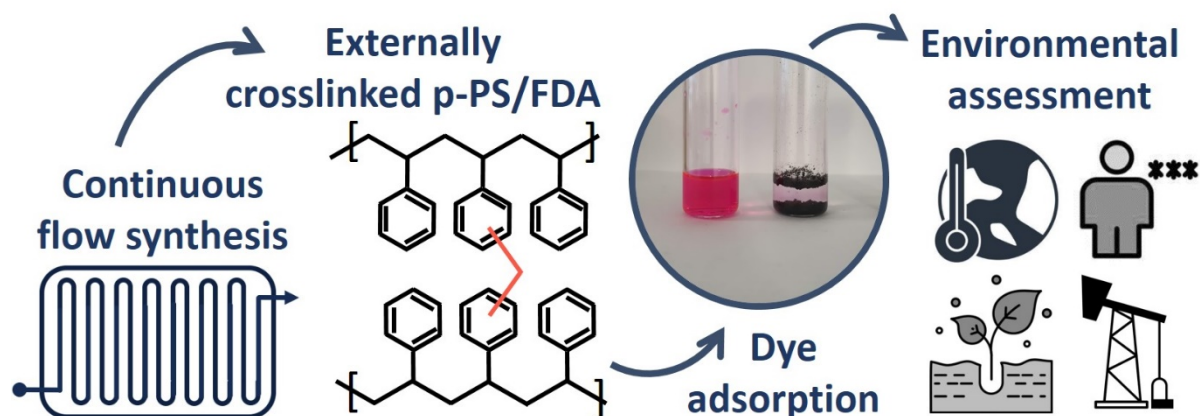
ρ [kg m⁻³] is fluid density, which is 1183 kg m⁻³

After substituting with values, we got the solution of $Re = 6524$.

Purification of synthesised HCP product

The solid product obtained after the washing and filtrating steps was considered to be entirely HCP. Unconverted reagents, namely DCX and PS, are soluble in DCE and should be washed away in liquid form during these stages. The only by-product from the reaction is either hydrochloric acid or water in gas form. Therefore, the final HCP product was considered to be of 100 % purity.

4. Environmental impacts of HCP continuous flow synthesis for dye adsorption



Graphical abstract - Conceptual idea for the environmental assessment of HCP continuous flow synthesis for dye adsorption

4.1. Introduction

In recent years, growing environmental concerns have compelled both commercial and academic sectors to prioritise the environmental impact of their activities. Minimising environmental impacts has become a policy for many companies, even in the early stages of technology development. This commitment extends to the academic researches, including the development of continuous flow HCP synthesis, which is the process that aiming to scale up for manufacturing in the future.

In the first objective of this study, a continuous flow approach for HCP synthesis was successfully implemented, as well as assessing product quality and productivity compared to batch synthesis. In this study, the focus was shifted to evaluating the environmental impacts of continuous flow synthesis of HCPs in comparison with batch synthesis. The subject of the study was the external crosslinking approach. Externally crosslinked HCP was selected due to its highest BET surface area among all three HCP species. The evaluation methodology employed for this study was life-cycle assessment (LCA) with two primary aims. The first aim pinpointed the hotspots, which were the main causes of environmental impacts, for each synthesis method. To achieve this, the environmental assessment using a functional unit of 1.5 g of synthesised HCPs was conducted. The second aim seek to quantify the disparities in environmental impacts between batch and flow synthesis of HCPs when serving for dye adsorption applications. Commercial HCPs are commonly employed in water treatment applications such as water purification,^{8, 11, 34, 50-53, 55} pesticide removal,²⁰ and dye removal,^{14, 34, 49, 54, 55} highlighting the versatility of HCPs in various utilisations.

To showcase this versatility in the context of the environmental assessments, two LCA sub-cases corresponding to two different dye types, Rhodamine B (RB) and Uniblue A (UA), were performed. These assessments were based on the 1.21 g and 1.27 g of adsorbed RB and UA molecules, respectively. The difference in adsorption capacity led to varying amounts of HCPs synthesised from batch and flow methods, due to their distinct textural properties. As

shown in the study for the first objective, flow-synthesised externally crosslinked HCP exhibited a lower CO₂/N₂ selectivity than batch-synthesised HCP by 22.6 %, resulting from its lower BET surface area compared to HCP from batch synthesis by 6 %. The environmental impact assessment relied on IMPACT 2002+ method, reporting fifteen midpoint impacts which can be grouped into four endpoint categories: Climate change, Resources, Ecosystem quality, and Human health. Each endpoint impact was presented as normalised scores, with an increase in scores indicating worsened environmental impact and a decrease in scores indicating higher environmental friendliness of the process. The results of this study revealed the major causes of environmental impacts for each synthesis method, explaining why flow synthesis may be more environmentally friendly than batch synthesis. Additionally, it specifically validated that flow synthesis is more environmentally friendly than batch synthesis for dye adsorption applications.

4.2. Discussion highlight, limitations, and conclusions

Regarding the first aim of this LCA study, the environmental assessment based on 1.5 g of externally crosslinked HCPs revealed that electricity consumption was the highest contributing factor of environmental impacts in batch synthesis. Transitioning to flow synthesis, electricity consumption was reduced correspondingly to the 95 % reduction in reaction times. This resulted in an 86.7 % decrease in normalised midpoint impact scores, particularly for top three midpoint impacts consisting of Respiratory inorganics, Global warming, and Non-renewable energy. Conversely, a primary impact contribution in flow synthesis was attributed to DCE consumption. While electricity consumption was lower in flow synthesis than in batch synthesis, chemical consumption had increased by 37.2 % due to the lower yield of external crosslinking in the continuous flow reactor by 42.1 %. Nevertheless, the overall environmental impact scores of continuous flow synthesis for all four endpoint impacts, which were Human health, Ecosystem quality, Climate change, and Resources remained lower than those of batch synthesis by 56 %, 11 %, 71 %, and 65 %, respectively. This underscored the benefit of flow synthesis for HCPs, demonstrating its potential to create fewer negative environmental impacts compared to traditional batch synthesis, considering the same amount of synthesised HCPs. However, it is crucial to acknowledge that this analysis did not account for potential performance differences in HCPs between batch and flow synthesis due to their distinct textural properties.

In pursuit of the second goal of this LCA study, isothermal dye adsorption experiments were conducted to assess the adsorption capacity of HCPs from batch and flow synthesis. The required amounts of HCPs were then calculated using the Langmuir model to fit the experimental adsorption isotherm data. Due to the poorer adsorption capacity of flow-synthesised HCP, the required amounts of flow-synthesised HCP for adsorbing 1.21 g RB and 1.27 g UA were 36 % and 43 % higher, respectively, compared to batch-synthesis HCP. This led to smaller reductions in the overall environmental endpoint impact scores compared to the scores of the LCA case from the first goal. The Ecosystem quality endpoint impact score increased by 20 % and 27 % for RB and UA adsorption applications when using flow synthesis. While Human health, Climate change, and Resources were reduced by 41 %, 61 %, and 53 % for RB adsorption, and by 37 %, 59 %, and 50 % for UA adsorption. Nevertheless, the overall

endpoint impact scores of HCP from flow synthesis still demonstrated that flow synthesis offers lower overall environmental impacts than batch synthesis, supporting the environmental benefits of implementing flow technique in HCP synthesis on a manufacturing scale.

To enhance the accuracy of this environmental impact assessment, future work should consider the regeneration of HCPs. Typical adsorbents, like HCPs, can be used across multiple cycles, potentially reducing the overall environmental impact despite increased chemical and energy consumption during the extra regeneration stage. This would require additional experiments involving several cycles of adsorption and desorption. Furthermore, assessing the environmental impacts of a scale-up continuous flow synthesis process should incorporate all relevant elements, for instance cleaning solvents, electricity for drying, infrastructures, including disposal process. Technoeconomic assessment (TEA) could also be included to evaluate economical aspects of scaling up continuous flow HCP synthesis.

As we continue to refine the flow synthesis of HCPs, it is essential to integrate environmental considerations into the process design and implementation. While this study demonstrated the environmental sustainability of continuous flow HCP synthesis serving for dye removal, further research is needed to evaluate the versatility of HCPs in other applications, considering both performance and environmental impact. By doing so, future manufacturing scale-up of flow synthesis would be ensure to align with sustainability objectives, enabling companies to meet their environmental responsibilities while expanding their competitiveness in the other markets serving for different utilisations.

Analyzing Environmental Impacts of Hypercrosslinked Polymers Produced from Continuous Flow Synthesis for Water Treatment

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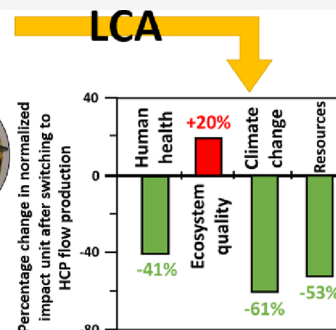
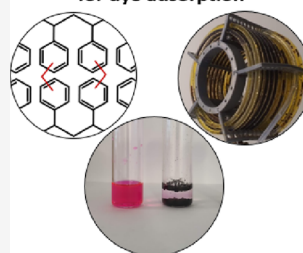
Article Recommendations



Supporting Information

ABSTRACT: Polymer production in the 21st century will require alternative approaches that do not impact the environment negatively. We recently reported that the synthesis of hypercrosslinked polymers (HCPs) *via* continuous flow synthesis required less than 99% of the time required in conventional batch reactions. However, the impact of deploying flow synthesis of HCPs and their application on the environment remain unknown. Here, we assessed the environmental impacts of HCP synthesis *via* batch and flow reactions and their application in water treatment through life-cycle assessment (LCA). These impacts were represented as normalized scores in four end point impact categories: Human health, Ecosystem quality, Climate change, and Resources. Yielding the same amount of HCPs, flow synthesis demonstrated lower end point impacts in all categories. This was due to consuming only 5% of the electricity required for batch reactions. As the specific surface areas of flow-produced HCPs were lower than those of batch-produced HCPs, 36% more flow-produced HCPs were required to remove Rhodamine B (RB) and Uniblue A (UA) dyes from water. Despite this limitation, using flow-produced HCPs for water treatment still scored lower overall negative environmental impacts when compared to batch-produced HCPs. Outcomes from this work showed that flow synthesis could enhance the sustainability of scale-up HCP production.

Continuous flow synthesis of hypercrosslinked polystyrenes for dye adsorption



1. INTRODUCTION

Continuous flow synthesis has been widely employed for process intensification in the production of fine chemicals¹ and pharmaceuticals² in the last two decades.³ Compared with batch reactors, flow reactors possess a higher surface area to volume ratio⁴ that improves heat and mass transfers, which enhances reaction kinetics.^{5,6} Other advantages associated with flow synthesis include ease of scale-up⁷ and safer reactions that involve hazardous chemicals or harsh operating conditions.⁸

Continuous flow reactions have also been exploited for synthesizing microporous materials, such as metal–organic frameworks (MOFs),⁷ covalent organic frameworks (COFs),⁹ and polymers of intrinsic microporosity (PIMs).¹⁰ We recently demonstrated that hypercrosslinked polymers (HCPs) could be synthesized¹¹ and optimized¹² *via* continuous flow reactions. HCPs are polymeric microporous adsorbents that possess extensive rigid yet flexible crosslinked structures that expand while adsorbing organic solvents.¹³ The advantages of synthesizing HCPs in flow reactors include (1) reducing synthesis duration by more than 99% and improving space–time yield (STY) by 32-fold, (2) improving reaction kinetics to yield HCPs with higher microporosity when compared to those synthesized in batch reactors, and (3) improving CO₂/N₂ selectivity of HCPs by 9.5-fold. As such, continuous flow syntheses could potentially scale up the production of highly selective HCPs. Despite demonstrating the feasibility of

continuous flow synthesis of HCPs, the sustainability of this process has not been evaluated. For example, other than improving productivity rates, will reducing synthesis duration benefit the environment? Will the lower specific surface areas of flow-produced HCPs create negative impacts on the environment when deployed in applications?

The most logical and scientific way to answer these questions and evaluate the sustainability of HCP flow syntheses towards the environment is to quantify the term “sustainability”. For example, life-cycle assessment (LCA) is widely used to assess the potential impact of processes based on quantitative modeling.^{14,15} Following the standard of the ISO 14040 and ISO 14044 frameworks,¹⁶ there are four stages in an LCA: Goal definition, Scope definition, Inventory analysis, and Impact assessment. Briefly, the study will clearly describe why an LCA is required. This would suggest what the functional unit of the LCA should be. The functional unit is the key quantified description to which all calculations will be

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referenced. The practitioner will then set up boundaries of the study consisting of foreground processes (visible processes where first-hand data could be retrieved by the practitioner) and elementary flows (resources, emissions, materials, waste, electricity, heating, etc.) showing as input and output flows. These flows will be categorized and summed up in an inventory table. Data from background processes (*i.e.*, upstream processes), usually retrieved from commercial databases, are also taken into account at this stage. Then, the analysis will be performed based on selected impact assessment methods that allow the practitioner to understand the environmental impacts and answer questions underpinning the intention that was defined at the start of the LCA design.

LCA has been utilized for evaluating various products, processes, or services. For instance, an LCA was performed for laboratory-scale graphene production with an intention to identify a production method with the lowest environmental impact from three different options that were based on small-scale process assessments.¹⁷ Meanwhile, an LCA was also performed to identify the most efficient and sustainable route for synthesizing porous polymers from Kraft black liquor.¹⁸ The motivation for performing this LCA was to evaluate if recycling and reusing solvents used in this process could lower its environmental impact when compared to the traditional process that currently uses single-use solvents. The LCA outcome showed that there were several trade-offs between these two scenarios, and neither scenario was the best in all impact categories. This showed that unless an LCA was performed, there is no way to verify if the alternative approach was indeed better than the original route. Vladislavljevic *et al.*¹⁹ performed an LCA to compare the environmental impacts of producing seven different amide-based polymer sorbents using a functional unit of 1 kg of captured CO₂. In this study, the authors put emphasis on the differences in adsorption capacity and selectivity between the proposed polymers and conventional molecularly imprinted polymers. Taking into account the adsorption performances of these sorbents, the LCA revealed that low quantities of HCPs were required to capture the same amount of CO₂ when compared to molecularly imprinted polymers, resulting in lower environmental impacts. By considering product utilization, this assessment evaluated more than half of the life cycle of the products.

Besides gas separation, HCPs have also been deployed as adsorbents in water treatment,^{20,21} removing ecotoxic dyes from the wastewater effluent from several industries.^{22–24} Examples of such dyes include Rhodamine B (RB), a magenta-colored, carcinogenic, and neurotoxic dye commonly found in textiles, paints, and fireworks,^{25,26} and Uniblue A (UA), a blue-colored dye commonly used in the textile industry.²⁷ We recently also showed that waste expanded polystyrene (trade name Styrofoam) can be recycled into HCPs for removing these dyes from water, with adsorption capacities of RB and UA reaching values of 552 and 1098 mg g^{−1}, respectively.²³ However, the synthesis of these highly microporous HCPs from Styrofoam waste (Brunauer–Emmett–Teller surface area reaching 1250 m² g^{−1}) required 5 times more the reagents deployed in HCP synthesis from monomers. This may offset the sustainability of upcycling one of the last-recycled plastic waste into advanced materials for water treatment *via* adsorption. Moreover, the actual impact and benefits of this approach remain unknown.

In this work, we evaluated the environmental impacts of upcycling Styrofoam into HCPs *via* batch and flow reactions

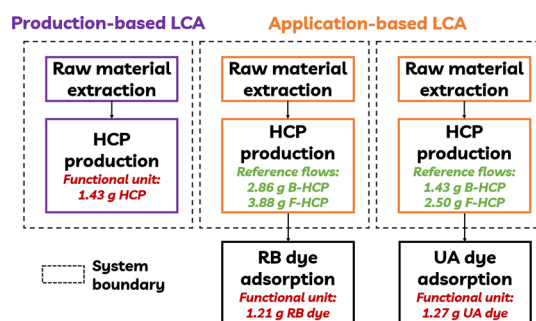
and their application in dye removal. This was achieved with two LCA main cases. The first LCA was based on the differences in synthesis methods: flow vs batch reactions. The goal of this LCA was to determine and compare the environmental impacts of producing approximately 1.5 g of HCPs *via* batch and flow reactions. The second LCA was application-based, focusing on evaluating the environmental impacts of deploying HCPs from batch or flow syntheses for dye removal *via* physisorption. This was based on the minimal amount of HCPs from each synthesis approach for removing about 1.2 g mL^{−1} of dyes. The scope of both LCAs was cradle-to-gate where the production of raw materials for HCP syntheses was also evaluated.^{19,28} The process was then modeled in the inventory analysis stage. We used the IMPACT 2002+ methodology for impact assessment, categorizing environmental impacts into four end-point-level impact categories: Human health, Ecosystem quality, Climate change, and Resources. Throughout these four categories of assessments, we determined how environmental impacts changed as a function of synthesis approach deployed in producing HCPs for water treatment. Outcomes from these studies demonstrated that continuous flow reactions improved the environmental impacts of HCP synthesis. The high productivity rates and improved environmental impacts of continuous flow synthesis suggested that this approach could be beneficial for HCP production at a mass manufacturing scale.

2. EXPERIMENTAL SECTION

2.1. Goal Definition. The aim of this work was to evaluate if continuous flow reactions improved the environmental impacts of HCP synthesis. Two LCAs were performed in this work. The first LCA was conducted to compare the difference in environmental impacts between conventional batch reactions and the new approach of flow synthesis based on the same quantity of HCPs produced from each method. The goal of this process based LCA was to identify the cause, *i.e.*, hotspots, of the environmental impacts of each synthesis approach and establish the differences in these impacts. The second LCA was performed to evaluate the difference in environmental impacts from the perspective of deploying the same amount of HCPs, produced from two different approaches, in dye adsorption for applications in water treatment. The goal of the second LCA was to elucidate if flow synthesis minimized the negative environmental impacts of HCP application despite requiring more materials due to the lower specific surface areas of flow-produced HCPs.

2.2. Scope Definition. The two LCA cases in this study were differentiated by their functional units (Scheme 1). The

Scheme 1. Functional Units and Reference Flows of Production-Based LCA and Application-Based LCA



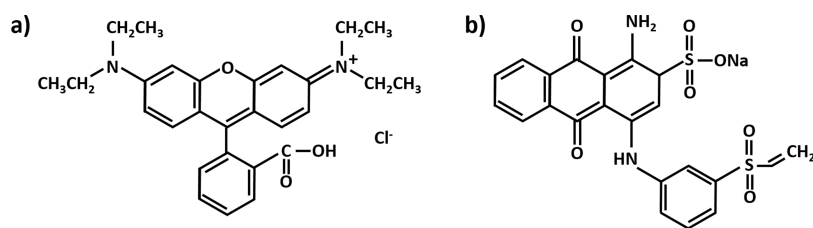


Figure 1. Dye molecules: (a) Rhodamine B (RB) and (b) Uniblue A (UA).

reason for two separated functional units was to answer whether, in case flow synthesis shows less environmental impacts than batch synthesis for the same amount of synthesized HCP, flow synthesis would still create less impacts when the amount of synthesized HCP is different between batch and flow reactions (which causes the difference in performance ability). The type of HCP selected for this study was derived from polystyrene that was externally crosslinked using formaldehyde dimethyl acetal (FDA). Batch-produced HCP and flow-produced HCP were denoted as B-HCP and F-HCP.

The functional unit of the process-based LCA was set to 1.43 g of HCP synthesized from batch and flow reactions. In the second LCA, two subcases were conducted representing two scenarios in which HCPs were utilized for removing RB and UA from water *via* adsorption (Figure 1). The functional units of these two LCA subcases were assigned as removing 1.21 g of RB and 1.27 of UA from water using B-HCP and F-HCP. On the basis of isothermal adsorption analyses (see the Supporting Information), the required masses of B-HCP and F-HCP for adsorbing 1.21 g of RB dyes were 2.86 and 3.88 g, respectively. Similarly, for adsorbing 1.27 g of UA dye, 1.43 g of B-HCP and 2.05 g of F-HCP were required.

The system boundaries of our LCAs (inside the dotted boxes in Schemes 1 and 2) included only raw material extraction and HCP synthesis stages. The inlet and outlet flows of the dye adsorption stage were omitted from environmental impact assessments here. This was due to the objective of the study to put emphasis on the comparison of environmental impacts created from the synthesis of HCPs between batch and flow reaction. Waste disposal, adsorbent regeneration, and

solvent recycling stages were negligible. We also excluded the impacts of material transport and infrastructure processes from these studies because of the lack of precise information associated with these factors. Although the production of HCPs was achieved through lab-scale experiments at the School of Engineering, The University of Edinburgh, some inputs such as raw chemicals and electricity were produced within the E.U. Hence, the geological scope in this work was European.

2.3. Inventory Analysis. 2.3.1. Foreground Processes.

Here, we regarded the synthesis stage as the foreground process. This inferred that primary data such as chemical and electricity consumption were collected directly from the laboratory. The total electricity usage was measured using an RS PRO digital plug-in energy meter (RS 178-5373).

The procedure for batch synthesis was as follows: Waste-expanded polystyrene (WEPS) was dissolved in 1,2-dichloroethane (DCE) in a 250 mL three-neck round flask. Iron(III) chloride (FeCl_3) and formaldehyde dimethyl acetal (FDA) were added into the mixture. A water-cooled condenser column was used to create a reflux system so that evaporated DCE could be condensed and reused in the reaction. Then, the mixture was heated at 80 °C while stirring with magnetic stirrer. We observed that gelation of this mixture occurred after 20–30 min of the reaction. This was common in batch HCP synthesis as the newly formed microporous HCPs adsorbed solvent molecules. At this point, we added 10–50 mL of DCE into the reactor, breaking up the gel so that stirring could carry on. After 24 h, the batch reaction was stopped by allowing the mixture to cool down to room temperature (25 °C). A sludge product was obtained, filtered, and washed with chloroform, excess methanol, and excess acetone consecutively. Then, the washed product was soaked in methanol overnight. Finally, the product was dried in an oven at 60 °C overnight.

The procedure for flow synthesis was as follows: Substrate feed was prepared by dissolving WEPS in DCE. This solution was loaded into a syringe prior to feeding into a polytetrafluoroethylene tube reactor (30 mL reactor volume, 1.58 mm inner diameter tube)¹² that was submerged in a 70 °C oil bath *via* a syringe pump (Cole-Parmer SP210iwz). A catalyst feed solution was prepared by mixing FeCl_3 and FDA in a separate solution of DCE. The catalyst feed was fed into the flow reactor *via* a peristaltic pump (SEKO Kronos 50). Both substrate and catalyst solutions were fed into the reactor, *via* a Y-junction where these solutions were mixed, with a total flow rate of 1.94 mL min⁻¹. Solid particles were extruded from the end of the reactor as a brownish sludge in the glass container at the end of the tube. The sludge product from flow synthesis was filtered, washed, and dried in the same method as the sludge product from batch synthesis.

2.3.2. Background Processes. Data for raw material extraction stage were obtained from ecoinvent 3, a Swiss-based commercial database that provided the models of

Scheme 2. Details of Inlet and Outlet Flows across the System Boundary of All LCAs in This Study

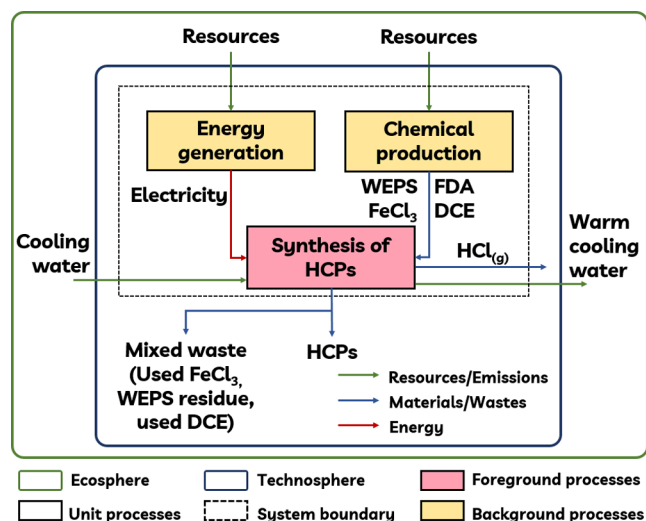


Table 1. Details of Data Collection Stage

products/services	processes	specificities	sources	accesses
batch-produced HCPs	Friedel–Crafts alkylation	very high	LCA practitioner	first-hand gathering
flow-produced HCPs	Friedel–Crafts alkylation	very high	LCA practitioner	first-hand gathering
expanded polystyrene (WEPS)	suspension polymerization of ethylene and benzene	medium	ecoinvent 3	database search
ethylene dichloride (DCE)	direct chlorination of ethylene	medium	ecoinvent 3	database search
iron(III) chloride (FeCl ₃), without water, in 40% solution state	oxidization of iron scape and FeCl ₂ with chlorine gas	medium	ecoinvent 3	database search
electricity, medium voltage	natural gas (conventional power plant), hard coal, nuclear (pressure water reactor), etc.	medium	ecoinvent 3	database search
formaldehyde dimethyl acetal (FDA)	condensation from methanol and formaldehyde	low	previous LCI literature	online journal search ²⁹

approximately 12,500 processes, ranging from solvent production to electricity generation in various regions to transportation. These models contained mathematical inputs (resources) and outputs (emission) produced from the process. However, a model of the FDA production process was not available in this database. Hence, this process was created manually by importing inventory data related to this process from another relevant LCA study.²⁹

2.3.3. Dye Adsorption Test. To conduct the second LCA, isothermal dye adsorption experiments were performed to determine the required quantities of B-HCP and F-HCP for RB and UA adsorption. The procedure was described as follows: Dye solutions were prepared at different concentrations within the range of 20–1000 mg L⁻¹ by dissolving dye powders in deionized water. HCP samples (5 g) were added into 5 mL of dye solutions of each concentration. These mixtures were left undisturbed until the equilibrium state was reached. The remaining dye concentration in these solutions was determined using a UV–vis spectrometer. The empirical adsorption isotherm was plotted between the equilibrium adsorption capacity, Q_e [mg g⁻¹], and the equilibrium dye concentration, C_e [mg L⁻¹]. C_e referred to the concentration of the remaining dye solutions, whereas Q_e was determined with the following equation:

$$Q_e = (C_0 - C_e) \frac{V}{m}$$

It should be noted that C_e was not an independent variable in the adsorption test; thus, the range of C_e would be different for each adsorption test (different HCP types in different dyes).

Langmuir and Freundlich adsorption isotherms were fitted to determine if dye adsorption in B-HCP and F-HCP was monolayer or multilayer. The equations were as follows:

$$\text{Langmuir adsorption: } Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

$$\text{Freundlich adsorption: } Q_e = K_F C_e^{1/n}$$

C_0 [mg L⁻¹] was the initial concentration of the dye solution, V [mL] was the volume of the dye solution, m [mg] was the mass of the HCP sample, K_L [L mg⁻¹] was the Langmuir constant associated with the binding energy that indicated how strong the interaction between dye molecules and the HCP surface is, Q_m [mg g⁻¹] referred to the maximum adsorption capacity, K_F [L^{1/n} mg^{1-1/n} g⁻¹] was the Freundlich constant related to adsorption capacity, and $\frac{1}{n}$ was the Freundlich

constant related to sorption intensity. As Langmuir and Freundlich adsorption models are empirical formulas, the values of K_L , Q_m , K_F , and $\frac{1}{n}$ parameters were then determined through the regression method.

2.4. Impact Assessment. We deployed the black-box tool to calculate the environmental impacts using the IMPACT 2002+ V2.11 assessment tool.³⁰ This method was chosen here as it had been used in a similar LCA that focused on the production of hypercrosslinked methacrylamide.¹⁹ This method provided 15 midpoint impact categories: Aquatic acidification, Aquatic eutrophication, Ozone layer depletion, Mineral extraction, Ionizing radiation, Aquatic ecotoxicity, Land occupation, Respiratory organics, Terrestrial ecotoxicity, Terrestrial acidification/nitrification, Noncarcinogens, Carcinogens, Respiratory inorganics, Global warming, and Non-renewable energy. These midpoint categories can be grouped into four impact categories at the end point level: Human health, Ecosystem quality, Climate change, and Resources. The connection between impact categories at the midpoint and endpoint level is shown in the [Supporting Information](#).

Quantification of environmental impacts was presented here as normalized scores. The normalization in the IMPACT 2002+ method was determined by dividing the impact score by the total impacts within the same impact category per person per year. This step was automatically compiled *via* the modeling software.

3. RESULTS AND DISCUSSION

3.1. Process Model Description. The reliability of the data was measured from the start of the data collection stage. Hence, it was necessary to present the quality of the data, *i.e.*, the specificity, the sources, and the accessibility. [Table 1](#) shows the description of the processes involved in this study and details of the data collection step. The excluded process was the transportation of reagents and solvents from the manufacturers to the laboratory. The physical infrastructure of the laboratory, *e.g.*, electricity for lighting and ventilation, was also excluded from the modeling.

Data from [Table 1](#) were combined to create a model that correlated to the goal and scope definitions of the LCA. The model for this LCA was conducted through SimiPro 8.0.3.14, an LCA modeling software that provides some life-cycle inventory databases and life-cycle inventory analysis methods.

3.2. Constraints and Assumptions. The constraints and assumptions from the life-cycle inventory analysis stage were outlined as follows: (1) Electricity and other utility consumptions during preheating and cleaning of equipment were exempted from the study. (2) Hydrochloric gas

byproduct was excluded because of the insignificant amount. The collection method and the quantity of hydrochloric gas produced from each synthetic approach are reported in the [Supporting Information](#). (3) WEPS residual after the filtration stage was negligible. (4) Electricity consumption in the drying stage was excluded. (5) Temperature change between inlet and outlet cooling water was negligible.

3.3. Production-Based LCA: the Comparison of Environmental Impact from the Production of 1.43 g of HCP via Batch and Flow Syntheses. **3.3.1. Life-Cycle Inventory.** The inventory data for the first LCA are shown in [Table 2](#). The aim of this LCA was to identify the differences in

Table 2. Inventory Items for the First LCA Study in Which the Functional Unit Was the Synthesis of 1.43 g of HCPs

subject	unit	batch	flow
products			
HCPs	g	1.43	1.43
chemicals			
WEPS	g	0.914	1.25
FeCl ₃	g	4.57	6.27
FDA	g	4.57	6.27
DCE	g	150	206
other utilities			
electricity	kWh	2.30	0.203
cooling water	m ³	0.864	N/A

environmental impacts of HCP synthesis *via* batch and flow reactions. The functional unit in this case was chosen as 1.43 g of HCPs. Synthesizing this amount of HCPs in batch and flow reactions required 24 h and 1 h and 40 min, respectively.

3.3.2. Impact Assessment. The midpoint level impact representing the intermediate position on the impact pathway was used for hotspot investigation. The top three midpoint categories with the highest impact scores from batch and flow syntheses of 1.43 g of HCPs ([Figure 2](#)) were Nonrenewable

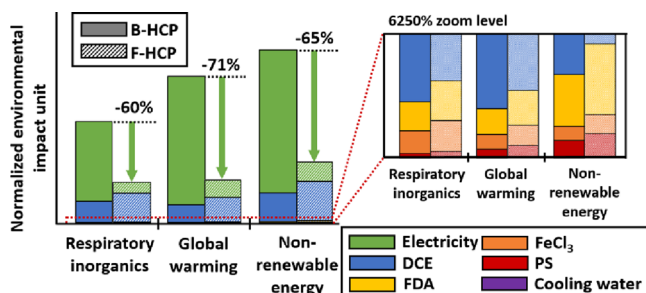


Figure 2. Top three environmental midpoint category impacts of the first LCA study in which the functional unit is the production of 1.43 g of HCP. Opaque bar charts refer to impacts from the synthesis of B-HCP. Stripe pattern bar charts refer to impacts from the synthesis of F-HCP.

energy, Global warming, and Respiratory inorganics. Each total impact unit was split into several color blocks to indicate the impact contribution of all elementary flows, *i.e.*, chemicals and utilities in the system.

We observed a huge score gap in the three midpoint impacts of Nonrenewable energy, Global warming, and Respiratory inorganics between batch and flow syntheses. Electricity was the major contributor of these gaps as the impact scores of those three highest midpoint impacts created from electricity

consumption in flow production were lower by 86.7% for all three mentioned impacts. This was reasonable as synthesis duration of batch reactions was 95% more than flow synthesis, hence consuming more electricity for heating. As electricity is mostly generated from primary nonrenewable energy, *i.e.*, natural gas (the proportion of resources for electricity generation is shown in the [Supporting Information](#)), electricity consumption here could be quantified by the equivalent units of resource consumption and emissions, *i.e.*, emitted CO₂ and PM_{2.5}.

DCE use in flow synthesis of HCPs generated higher impacts in several categories when compared to batch synthesis. The impact scores of Nonrenewable energy created by DCE in flow synthesis were 37.2% higher than those in batch reactions. This was because the HCP yield from flow synthesis was 42.1% lower than those of batch reactions. As such, according to [Table 2](#), more reagents were used to synthesize 1.43 g of HCPs in flow reactions; hence, more DCE was consumed. Although the impact contribution from reactants was also higher in flow synthesis, they were insignificant compared to the impacts created from solvents after the normalization of impact scores.

The environmental impacts at the end point level in [Figure 3](#) indicated that flow synthesis created a lower impact in all end

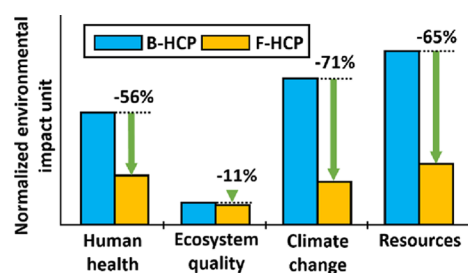


Figure 3. Normalized end-point-level impact assessments of the first LCA study in which the functional unit is the production of 1.43 g of HCP.

point categories when compared to batch reactions. The largest decrease was the impact toward Climate change that was reduced by 71%, followed by a 65% decrease in Resources and a 56% reduction in Human health. The large gaps in these three end point impacts were related to the high normalized midpoint category impact unit of Nonrenewable energy, Global warming, and Respiratory inorganics, respectively, as mentioned earlier. The smallest reduction in environmental impact was in Ecosystem quality; flow reactions only reduced this factor by 11%. This proved that flow synthesis of HCPs did not negatively affect the environment as much as traditional batch synthesis of the same amount of HCPs, offering a more sustainable approach to synthesize HCPs. However, this does not mean that application of flow-synthesized HCPs would reduce the environmental impacts.

3.4. Application-Based LCA: Environmental Impact from the HCP Synthesis for Dye Adsorption.

3.4.1. Dye Adsorption Performance. The second LCA study aimed to determine and compare the environmental impacts created from batch and flow syntheses of the required amount of HCPs for removing the same amount of RB and UA from water *via* adsorption. Isothermal dye adsorption experiments were conducted to determine the maximum adsorption capacity of B-HCP and F-HCP for each dye type. These

values were then used to calculate the required amount to adsorb an amount of dye (the functional unit of the second LCA study). Curve fitting of experimental adsorption isotherm data of B-HCP and F-HCP using Langmuir and Freundlich models shown in Figure 4 was used here to evaluate the

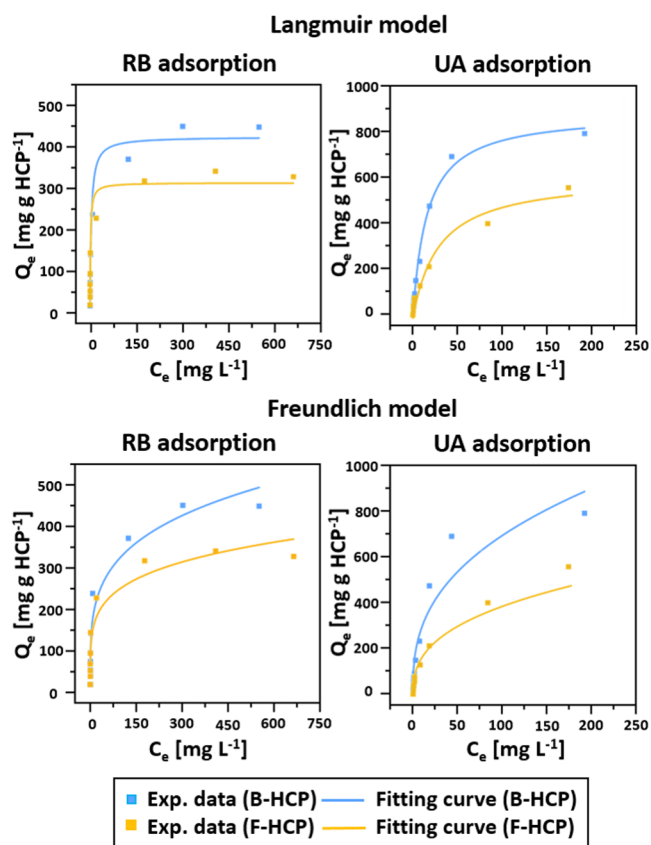


Figure 4. Adsorption isotherms.

adsorption behavior of these HCP samples. Clearly, the equilibrium dye concentration of the UA solution was lower than that of the RB solution, indicating that HCPs adsorbed more UA molecules than RB molecules. With higher R^2 values (Table 3), the Langmuir model was able to describe the dye

Table 3. Adsorption Isotherm Parameters

dyes	synthetic methods	Langmuir model			Freundlich model		
		K_L	Q_m	R^2	K_F	$1/n$	R^2
RB	batch	0.245	424	0.967	106	0.243	0.952
	flow	0.613	313	0.958	98.1	0.204	0.920
UA	batch	0.062	887	0.992	123	0.376	0.903
	flow	0.035	619	0.978	77.7	0.353	0.960

adsorption behavior of both B-HCP and F-HCP. This indicated that the adsorption behavior of all HCPs was homogeneous, in which the adsorption capacity was limited when all sorption sites are nonvacant (monolayer adsorption).²³ The adsorption behavior of B-HCP and F-HCP in RB and UA solutions, *i.e.*, maximum adsorption capacity (Q_m), was used here in this work to calculate the required amount of HCPs for dye adsorption.

3.4.2. Life-Cycle Inventory. The inventory data for the second LCA that assessed the environmental impacts of using

the minimum amount of B-HCP and F-HCP to adsorb RB and UA dyes are shown in Table 4. The functional units in the two

Table 4. Inventory Items for the Second LCA Study in Which Environmental Impacts Were Assessed on the Production of the Required Amount of B-HCP and F-HCP for 1.21 g RB and 1.27 g UA Adsorption

subject	unit	RB (1.21 g)		UA (1.27 g)	
		batch	flow	batch	flow
<i>products</i>					
HCPs	g	2.86	3.88	1.43	2.05
<i>chemicals</i>					
WEPS	g	1.83	3.39	0.914	1.80
FeCl ₃	g	9.14	17.0	4.57	8.98
FDA	g	9.14	17.0	4.57	8.98
DCE	g	300	557	150	295
<i>other utilities</i>					
electricity	kWh	4.59	0.497	2.30	0.277
cooling water	m ³	1.73		0.864	

subcases were removing 1.21 g of RB and 1.27 g of UA from 12 L of water *via* adsorption with B-HCP and F-HCP. The required weights of B-HCP and F-HCP then became reference flow inputs of the second LCA model. According to the selected functional unit, the required amounts of B-HCP and F-HCP were 2.86 and 3.88 g, respectively, for RB adsorption and 1.43 and 2.05 g, respectively, for UA adsorption (Scheme 1).

3.4.3. Impact Assessment. The life-cycle impact assessments for the two subcases of the second LCA study are presented as normalized end point category impacts in Figure 5. According to Table 4, the amounts of F-HCPs used for RB and UA adsorption were higher than those of B-HCPs by 36 and 43%, respectively. This was ascribed to their lower adsorption capacity (Table 3). Hence, the difference in impact scores between batch and flow was different from the first LCA case. The impacts of Climate change, Resources, and Human

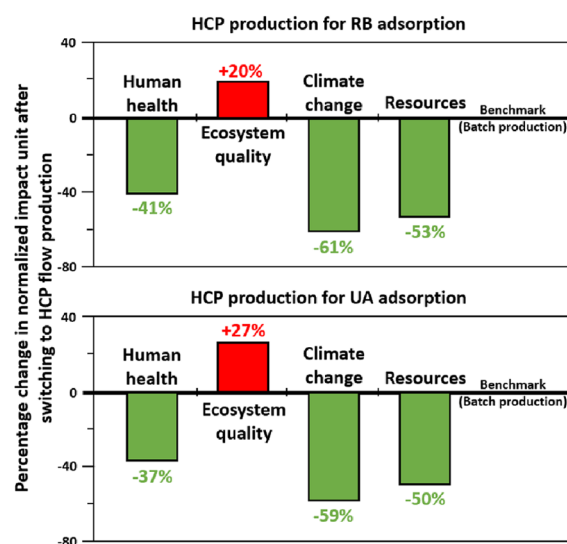


Figure 5. Percentage changes in normalized end point category impacts from HCP production after switching to the flow approach. The functional unit is based on 1.21 g of RB and 1.27 g of UA to be adsorbed.

health for flow synthesis of 3.88 g of F-HCPs were 61, 53, and 41% lower than those from batch synthesis of 2.86 g of B-HCP for adsorbing 1.21 g of RB. Similarly, the impacts toward these three impact categories for adsorbing 1.27 g of UA dye with 2.05 g of F-HCPs were 59, 50, and 37% lower than using 1.43 g of B-HCPs. This could be due to the impact associated with electricity consumption (which was the major contributor according to the first LCA result) in the production of B-HCP. This highlighted the advantage of flow synthesis as this approach could create lower environmental impacts in terms of Climate change and Resources while producing more product. Meanwhile, the impact scores of Ecosystem quality from flow-produced HCPs for RB and UA adsorption were higher than those of HCPs yielded from batch reactions by 20 and 27%, respectively. However, the score from this category was still relatively low when compared to the normalized scores of the other three end-point-level impacts.

4. CONCLUSIONS

The comparison of environmental impacts of HCP production between traditional batch and flow syntheses was revealed in this study to prove the sustainability of flow HCP synthesis. Through LCA, the impact assessment showed that on the basis of the production of 1.43 g of HCP, flow production provided lower impact scores in all four end-point-level categories, consisting of Human health, Ecosystem quality, Climate change, and Resources, by 56, 11, 71, and 65%, respectively. This was primarily due to the decrease in electricity consumption in flow production in which it required only 5% of traditional batch reaction time. The flow system also provided lower environmental impacts than the batch system when a higher amount of F-HCP was produced for dye adsorption application. When 1.21 g of RB and 1.27 g of UA needed to be adsorbed, F-HCP was required higher than B-HCP by 36 and 43%, respectively, as F-HCP had lower adsorption capacity. The impact scores of Climate change, Resources, and Human health from the production of 3.88 g of F-HCP were lower by 61, 53, and 41% than the production of 2.86 g of B-HCP for RB adsorption. The impact scores from the same three end point categories were similar in the adsorption of UA scenario, as the production of 2.05 g of F-HCP created lower scores than the production of 1.43 g of B-HCP by 59, 50, and 37%. There is a suggestion that become noticeable after the conduction of LCA to improve the level of sustainability of the flow process. Higher DCE consumption in flow production was observed in both assessments. This had a negative effect toward the Ecosystem quality category by 20 and 27% in RB and UA adsorption, respectively. The substitution of current halogenated solvent (DCE) to the environment-friendlier chemicals could help lower impacts created from the proposed flow production.

Moreover, there are several suggestions that can improve the reliability of the assessment. First, an uncertainty analysis and sensitivity study would confirm the reliability of the LCA model as the background process of FDA is missing from the ecoinvent database. Second, an environmental assessment of the pilot scale production should be conducted. This would require the validation of the pilot plant continuous flow reactor that should be redesigned and further investigated. Third, the regeneration of HCPs should be included in the study. This would lower the amount of utilized HCPs for the specific application. However, other elements involving the regeneration of such solvents or electricity might need to be

considered. Fourth, the heat transfer within the system could be reused from one place to other. This would help lower the input of heat of the whole system. Yet, the pilot scale flow synthesis process is required before this step could be conducted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.3c00829>.

The document includes (1) the pathway of the impact from IMPACT 2002+ method, (2) the description for the HCl gas collection experiment, (3) the inventory of the background processes from ecoinvent, (4) the UV–vis spectra and calibration curve of RB and UB dyes at different initial concentrations, and (5) the impact scores from three LCA cases (PDF)

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Author Contributions

The study was proposed by N.C. The conceptualized idea was discussed between N.C. and C.L. The experimental part (synthesizing HCPs and dye adsorption test) was conducted by N.C. Modeling of LCA and result analyzing were done by N.C. The paper was prepared by N.C. with supervision from C.L.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

HCP	hypercrosslinked polymer
LCA	life-cycle assessment
RB	Rhodamine B
UA	Uniblue A
B-HCP	batch-produced hypercrosslinked polymer
F-HCP	flow-produced hypercrosslinked polymer

WEPS waste-expanded polystyrene
DCE 1,2-dichloroethane
FeCl₃ iron(III) chloride
FDA formaldehyde dimethyl acetal

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Supplementary Information

Analyzing environmental impacts of
hypercrosslinked polymers produced from
continuous flow synthesis for water treatment

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Impact pathway from IMPACT 2002+ method

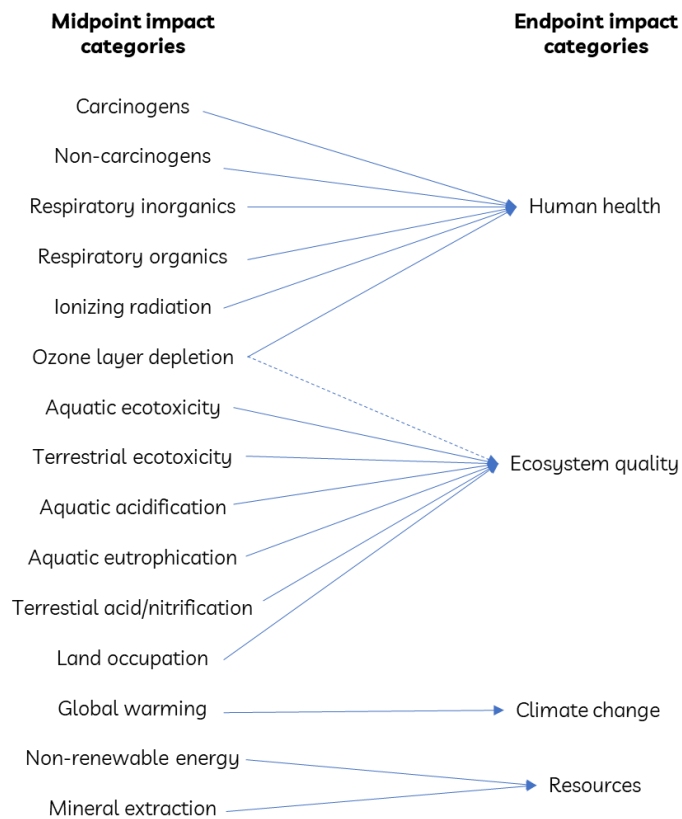


Figure S1 IMPACT 2002+ framework.¹ Dotted arrow represents uncertain impact pathway between midpoint and endpoint impact categories.

Additional experiment detail for HCl gas data collection

The amount of by-product from the main process released into the ecosphere could potentially contribute to a significant impact on some environmental categories if it accumulates in large-scale production. In this work, hydrogen chloride gas is a common by-product of the synthesis of HCPs via the Friedel-Crafts reaction. Data collection of HCl gas from the lab-scale production is thus conducted for the assessment, which could later lead to a rational assumption on how much different HCl gas is emitted between batch and flow synthesis of HCPs on a larger scale.

There are numerous observations about the existence of HCl gas in the system while producing HCPs, yet there is no exact quantitative information on how much HCl gas is generated. The closest report comes from HCP synthesis via solvent-free mechanochemical reactions, in which significant pressure increases due to the formation of HCl gas inside the milling vessel even with a small amount of monomer. With reagents and catalysts in our synthesis system, Figure S2 shows how by-product HCl gas is produced along with polystyrene-based HCPs.

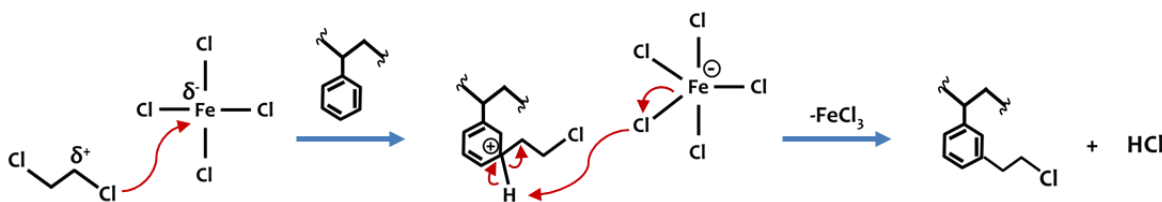


Figure S2 Production of HCl gas by-product

Although it is possible to approximate the amount of the generated by-product through a chemical equation, it is quite hard to do so when polystyrene is the substrate of the reaction due to the uncertain molecular weight. Back to the easiest way to gain the information, direct gas collection was conducted, which was differently adapted to suit two different synthesis methods, as shown in the schematic in Figure S3. Basically, HCl gas is transported through the tube

connecting on top of the cooling condenser in batch setup and the product container in flow setup to 100 mL of DI water in another flask. The pH change of DI water in the connected flask will change accordingly to the amount of dissolved HCl gas, which can be calculated through the following equation:

$$HCl \text{ weight [g]} = \left(10^{-pH} - 10^{-pH_0} \left[\frac{\text{mol } H_3O^+}{L} \right] \right) \times DI \text{ water volume [L]} \times \frac{1 \text{ mol } HCl}{1 \text{ mol } H_3O^+} \times 36.5 \left[\frac{g}{\text{mol } HCl} \right]$$

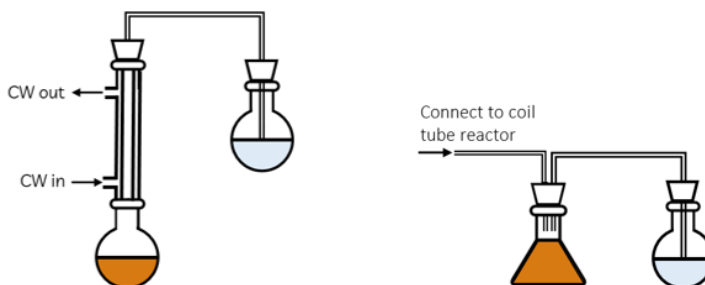


Figure S3 HCl gas collecting set-up for batch (Left) and flow (Right) synthesis method

Table S1. Inventory of background process (Ecoinvent database)

Products / Services	Inputs
Expanded polystyrene (WEPS)	Polystyrene, expandable {RER} production Alloc Def, U
Ethylene dichloride (DCE)	Ethylene dichloride {RER} production Alloc Def, U
Iron (III) chloride (FeCl ₃), without water, in 40% solution state	Iron (III) chloride, without water, in 40% solution state {GLO} market for Alloc Def, U
Trichloromethane (Chloroform)	Trichloromethane {RER} production Alloc Def, U
Methanol	Methanol {GLO} market for Alloc Def, U
Acetone	Acetone, liquid {RER} production Alloc Def, U
Electricity, medium voltage	Electricity, medium voltage {GB} market for Alloc Def, U
Cooling water	Water, cooling, unspecified natural origin, GB

Table S2. Inventory of background process (FDA production)²

Products	Amount	Unit
Dimethoxymethane {GB} production Alloc Def, U	1.0	kg
Inputs	Amount	Unit
Methanol {GLO} market for Alloc Def, U	0.842	kg
Formaldehyde {RER} oxidation of methanol Alloc Def, U	0.395	kg
Electricity, high voltage {GB} market for Alloc Def, U	0.0170	MJ
Heat, district or industrial, other than natural gas {RoW} market for Alloc Def, U	8.64	MJ

Table S3. Electricity (Medium voltage) generation resources (Ecoinvent database)

Products	Amount	Unit
Electricity, medium voltage {GB} market for Alloc Def, U	1.0	kWh
Inputs	Amount	Unit
Electricity, medium voltage {GB} market for Alloc Def, U	0.0024	kWh
Electricity, medium voltage {GB} electricity voltage transformation from high to medium voltage Alloc Def, U	1.0	kWh

Table S4. Electricity (Transformation from high to medium voltage) generation resources (Ecoinvent database)

Products	Amount	Unit
Electricity, medium voltage {GB} electricity voltage transformation from high to medium voltage Alloc Def, U	1.0	kWh
Inputs	Amount	Unit
Electricity, high voltage {GB} market for Alloc Def, U	1.0059	kWh

Table S5. Electricity (High voltage) generation resources (Ecoinvent database)

Products	Amount	Unit
Electricity, high voltage {GB} market for Alloc Def, U	1.0	kWh
Inputs	Amount	Unit
Electricity, high voltage {GB} market for Alloc Def, U	0.0273	kWh
Electricity, high voltage {GB} electricity production, hard coal Alloc Def, U	0.3095	kWh
Electricity, high voltage {GB} electricity production, hydro, pumped storage Alloc Def, U	0.0109	kWh
Electricity, high voltage {GB} electricity production, hydro, run-of-river Alloc Def, U	0.0137	kWh
Electricity, high voltage {GB} electricity production, natural gas, at conventional power plant Alloc Def, U	0.4364	kWh
Electricity, high voltage {GB} electricity production, nuclear, pressure water reactor Alloc Def, U	0.1322	kWh
Electricity, high voltage {GB} electricity production, oil Alloc Def, U	0.0151	kWh
Electricity, high voltage {GB} electricity production, wind, <1MW turbine, onshore Alloc Def, U	0.0017	kWh
Electricity, high voltage {GB} electricity production, wind, >3MW turbine, onshore Alloc Def, U	0.0034	kWh
Electricity, high voltage {GB} electricity production, wind, 1-3MW turbine, offshore Alloc Def, U	0.0047	kWh
Electricity, high voltage {GB} electricity production, wind, 1-3MW turbine, onshore Alloc Def, U	0.0090	kWh
Electricity, high voltage {GB} import from FR Alloc Def, U	0.0325	kWh

Electricity, high voltage {GB} import from IE Alloc Def, U	0.0004	kWh
Electricity, high voltage {GB} heat and power co-generation, biogas, gas engine Alloc Def, U	0.0131	kWh
Electricity, high voltage {GB} heat and power co-generation, wood chips, 6400kW thermal, with extensive emission control Alloc Def, U	0.0068	kWh
Electricity, high voltage {GB} treatment of blast furnace gas, in power plant Alloc Def, U	0.0026	kWh
Electricity, high voltage {GB} treatment of coal gas, in power plant Alloc Def, U	0.0008	kWh
Electricity, high voltage {GB} treatment of municipal solid waste, incineration Alloc Def, U	0.0071	kWh

UV-VIS spectra of dye solution at different initial concentration for producing calibration curve of RB and UA dye

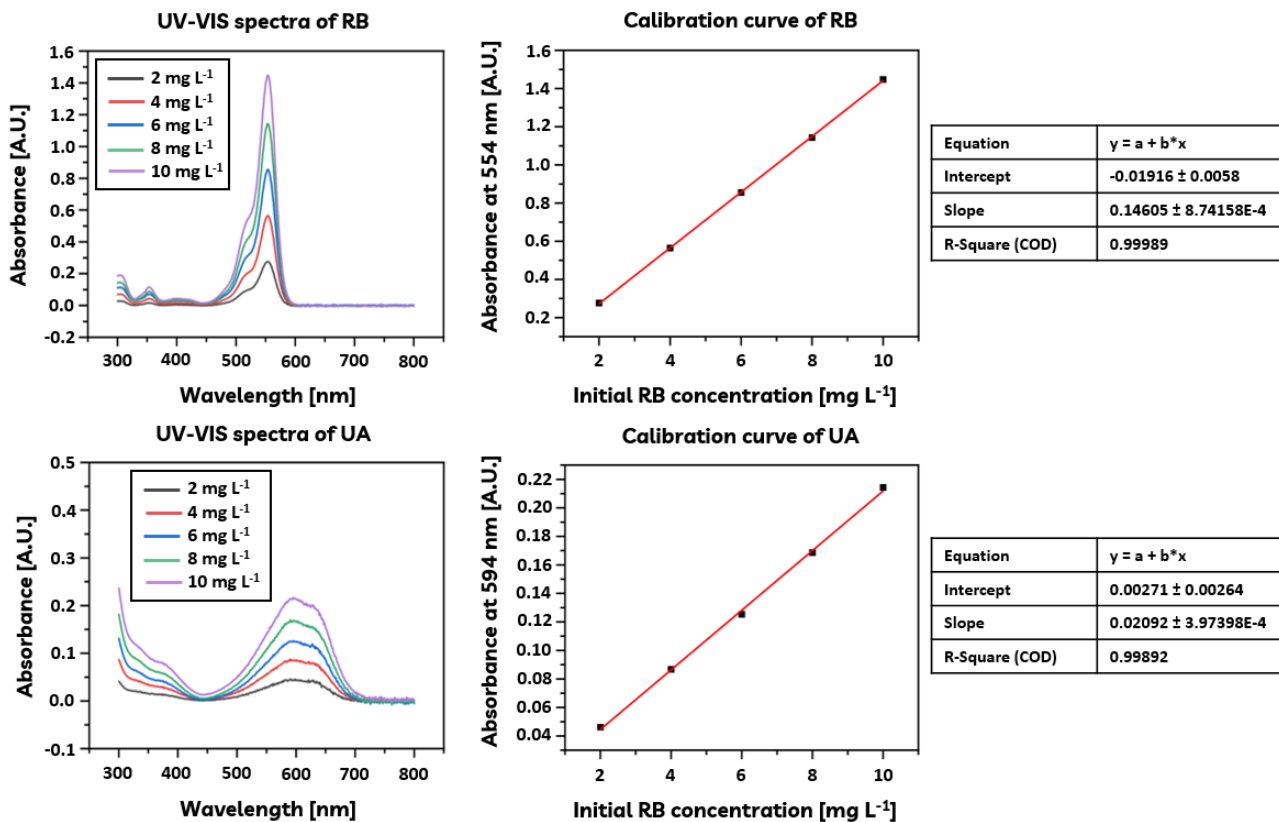


Figure S4 UV-VIS spectra and calibration curves of RB and UA. The maximum adsorbed amplitude of RB and UA is 554 and 594 nm.^{3,4}

Table S6. Midpoint characterization scores from the synthesis of 1.43 g HCPs

Midpoint impact categories	Unit	B-HCP	F-HCP
Aquatic acidification	kg _{eq} SO ₂ into air	8.57 x 10 ⁻³	2.94 x 10 ⁻³
Aquatic eutrophication	kg PO ₄ ³⁻ into water	2.46 x 10 ⁻⁴	1.04 x 10 ⁻⁴
Ozone layer depletion	kg _{eq} CFC-11 into air	1.63 x 10 ⁻⁷	1.24 x 10 ⁻⁷
Mineral extraction	MJ surplus energy	3.47 x 10 ⁻²	2.82 x 10 ⁻²
Ionizing radiation	Bq _{eq} C-14 into air	5.08 x 10 ¹	1.13 x 10 ¹
Aquatic ecotoxicity	kg _{eq} trithylene glycol into water	1.34 x 10 ²	1.24 x 10 ²
Land occupation	m ² _{eq} organic arable land-year	3.84 x 10 ⁻²	8.63 x 10 ⁻³
Respiratory organics	kg _{eq} ethylene into air	2.22 x 10 ⁻⁴	1.63 x 10 ⁻⁴
Terrestrial ecotoxicity	kg _{eq} trithylene glycol into soil	3.84 x 10 ¹	3.93 x 10 ²
Terrestrial acid/nutrification	kg _{eq} SO ₂ into air	2.39 x 10 ⁻²	8.60 x 10 ⁻³
Non-carcinogens	kg _{eq} chloroethylene into air	9.38 x 10 ⁻³	6.26 x 10 ⁻³
Carcinogens	kg _{eq} chloroethylene into air	1.71 x 10 ⁻²	1.78 x 10 ⁻¹
Respiratory inorganics	kg _{eq} PM2.5 into air	1.25 x 10 ⁻³	5.07 x 10 ⁻⁴
Global warming	kg _{eq} CO ₂ into air	1.76 x 10 ⁰	5.17 x 10 ⁻¹
Non-renewable energy	MJ total primary non-renewable	3.19 x 10 ¹	1.12 x 10 ¹

Table S7. Midpoint characterization scores from the synthesis of HCPs for 1.21 g RB dyes adsorption

Midpoint impact categories	Unit	B-HCP	F-HCP
Aquatic acidification	kg _{eq} SO ₂ into air	1.71 x 10 ⁻²	7.75 x 10 ⁻³
Aquatic eutrophication	kg PO ₄ ³⁻ into water	4.91 x 10 ⁻⁴	2.75 x 10 ⁻⁴
Ozone layer depletion	kg _{eq} CFC-11 into air	3.26 x 10 ⁻⁷	3.32 x 10 ⁻⁷
Mineral extraction	MJ surplus energy	6.92 x 10 ⁻²	7.59 x 10 ⁻²
Ionizing radiation	Bq _{eq} C-14 into air	1.10 x 10 ²	2.93 x 10 ¹
Aquatic ecotoxicity	kg _{eq} trithylene glycol into water	2.67 x 10 ²	3.35 x 10 ²
Land occupation	m ² _{eq} organic arable land-year	7.66 x 10 ⁻²	2.24 x 10 ⁻²
Respiratory organics	kg _{eq} ethylene into air	4.43 x 10 ⁻⁴	4.39 x 10 ⁻⁴
Terrestrial ecotoxicity	kg _{eq} trithylene glycol into soil	7.67 x 10 ¹	1.06 x 10 ²
Terrestrial acid/nutrition	kg _{eq} SO ₂ into air	4.78 x 10 ⁻²	2.27 x 10 ⁻²
Non-carcinogens	kg _{eq} chloroethylene into air	1.87 x 10 ⁻²	1.68 x 10 ⁻²
Carcinogens	kg _{eq} chloroethylene into air	3.42 x 10 ⁻²	4.81 x 10 ⁻²
Respiratory inorganics	kg _{eq} PM2.5 into air	2.50 x 10 ⁻³	1.35 x 10 ⁻³
Global warming	kg _{eq} CO ₂ into air	3.51 x 10 ⁰	1.36 x 10 ⁰
Non-renewable energy	MJ total primary non-renewable	6.36 x 10 ¹	2.97 x 10 ¹

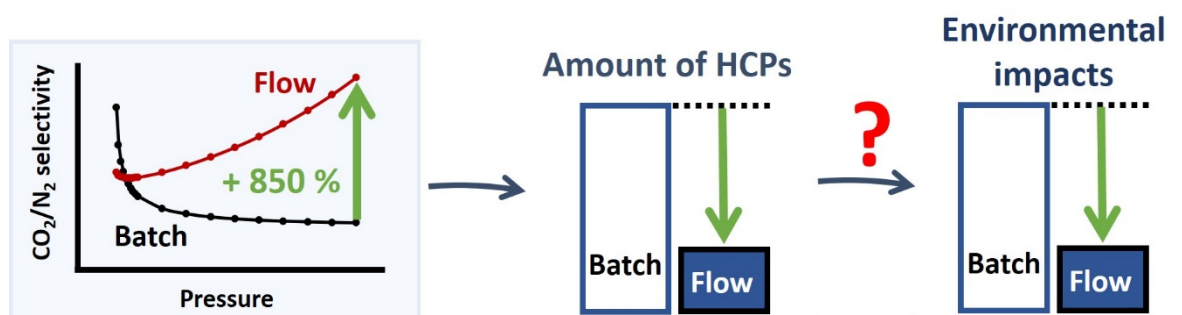
Table S8. Midpoint characterization scores from the synthesis of HCPs for 1.27 g UA dyes adsorption

Midpoint impact categories	Unit	B-HCP	F-HCP
Aquatic acidification	kg _{eq} SO ₂ into air	8.57 x 10 ⁻³	4.15 x 10 ⁻³
Aquatic eutrophication	kg PO ₄ ³⁻ into water	2.46 x 10 ⁻⁴	1.47 x 10 ⁻⁴
Ozone layer depletion	kg _{eq} CFC-11 into air	1.63 x 10 ⁻⁷	1.76 x 10 ⁻⁷
Mineral extraction	MJ surplus energy	3.46 x 10 ⁻²	4.03 x 10 ⁻²
Ionizing radiation	Bq _{eq} C-14 into air	5.08 x 10 ¹	1.59 x 10 ¹
Aquatic ecotoxicity	kg _{eq} trithylene glycol into water	1.34 x 10 ²	1.78 x 10 ²
Land occupation	m ² _{eq} organic arable land-year	3.84 x 10 ⁻²	1.21 x 10 ⁻²
Respiratory organics	kg _{eq} ethylene into air	2.22 x 10 ⁻⁴	2.33 x 10 ⁻⁴
Terrestrial ecotoxicity	kg _{eq} trithylene glycol into soil	3.84 x 10 ¹	5.63 x 10 ¹
Terrestrial acid/nutrition	kg _{eq} SO ₂ into air	2.39 x 10 ⁻²	1.22 x 10 ⁻²
Non-carcinogens	kg _{eq} chloroethylene into air	9.37 x 10 ⁻³	8.93 x 10 ⁻³
Carcinogens	kg _{eq} chloroethylene into air	1.71 x 10 ⁻²	2.55 x 10 ⁻²
Respiratory inorganics	kg _{eq} PM2.5 into air	1.25 x 10 ⁻³	8.93 x 10 ⁻³
Global warming	kg _{eq} CO ₂ into air	1.76 x 10 ⁰	7.28 x 10 ⁻¹
Non-renewable energy	MJ total primary non-renewable	3.19 x 10 ¹	1.59 x 10 ¹

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5. Environmental impacts of HCP continuous flow synthesis for CO₂ adsorption



Graphical abstract - Initial hypothesis of the third study

5.1. Introduction

As an environmental impact assessment considering the entire life-cycle of a process or service, different applications of the same product can result in varying environmental impacts. In the case of HCPs, their high specific surface areas make them competitive with other microporous adsorbent for various applications. Numerous literatures have reported that HCPs offer promising potential for CO₂ adsorption.¹⁻³ By studying the environmental impacts of flow-synthesised HCPs in diverse applications, for instance, dye adsorption and CO₂ adsorption, we can gain a comprehensive understanding of their overall environmental sustainability and contribute to sustainable practices in multiple industries and sectors.

In this study, the focus lied in conducting an environmental impact assessment by comparing the batch and flow synthesis of HCPs for atmospheric pressure CO₂ adsorption. The difference in BET surface area and porosity between HCPs synthesised through batch and flow processes affected their CO₂ and N₂ adsorption capacity and their CO₂/N₂ selectivity. This, in turn, influenced the amount of HCPs required to capture the same CO₂ amount, ultimately affecting the environmental impacts. Previous findings had shown that flow-synthesised internally crosslinking HCPs exhibited an 850 % higher CO₂/N₂ selectivity at 1 atm and 298 K compared to batch-synthesised internally crosslinked HCPs. Based on this, our initial hypothesis posited that internally crosslinking HCPs from flow synthesis would require a lower amount to capture the same CO₂, leading to lower environmental impacts than batch synthesis.

To assess these environmental impacts, LCA method was employed, consistent with the previous study for the second objective. For the purpose of comparing batch and flow synthesis, a functional unit was chosen involving the adsorption of 40 mg of CO₂ under conditions of 1 atm and 298 K. The required amounts of all three HCP types (internally, post-, and externally crosslinked) from both batch and flow synthesis were calculated based on gas adsorption data obtained in the previous study. This study adopted a cradle-to-gate system boundary, focusing on the production stages of HCPs, including upstream processes. Data was collected first-hand from laboratory experiments. The assessment method of IMPACT 2002+ was employed consistent to the previous study. The outcomes of the LCA intended to address

the goal of the study, which was to test our initial hypothesis regarding whether flow-synthesised internally crosslinked HCP offer lower environmental impacts compared to its batch counterparts due to its superior gas adsorption performance.

5.2. Discussion highlight, limitations, and conclusions

In assessing the gas adsorption capacity and CO₂ selectivity over N₂, it was observed that the required weight of flow-synthesised internally crosslinked HCP for 40 mg CO₂ caption was 36 % lower than the same HCP type produced through batch synthesis. Conversely, flow-synthesised HCPs from post- and external crosslinking approaches necessitated 41 % and 55 % more weight compared to batch synthesis, respectively. However, when evaluating environmental impacts, the post-crosslinking flow synthesis demonstrated reductions in endpoint impacts related to Climate change, Resources, and Human health with decreases of 70 %, 62 %, and 51 %, respectively. This marked the highest decrease among all three crosslinking approaches. The increase in Ecosystem quality endpoint impact by 9 % was also the lowest among the three approaches. In contrast, the flow synthesis of internal crosslinked HCP showed a reduction in Climate change and Resources by 36 % and 15 %, respectively, representing the lowest reduction among the three crosslinking approaches. Furthermore, it recorded the highest increases in Ecosystem quality and Human health, with the increments of 197 % and 19 %, respectively, compared to the other two approaches. These outcomes indicated that the superior CO₂ adsorption performance of internally crosslinked HCP from flow synthesis was not the main contributing factor to the overall reduction in environmental impacts. Instead, the key factor for achieving reduced environmental impacts was product yield. The 7 % product yield of the flow-synthesised internal crosslinking was 88 % lower than that of batch synthesis, resulting in higher chemical consumption and, consequently, higher environment burdens. Therefore, improving product yield is a critical step towards enhancing the environmental sustainability of the flow synthesis process.

Regarding the product yield of post-crosslinking using flow synthesis, which was still 18 % lower than batch synthesis, it was not necessary for the product yield of flow synthesis to be identical to that of batch synthesis. Since flow synthesis had also offered lower electricity consumption due to the shorter reaction time, determining the product yield threshold that balanced the increase in impact scores from increased chemical consumption and the decrease in impact scores from decreased electricity consumption was needed to achieve the flow process that offers lower environmental impacts for all four aspects than the batch synthesis. The ideal product yield of the internal crosslinking system using flow synthesis, the least environmentally sustainable system, was found at 25 %, which was a 250 % increment from the base case and was 57 % lower than the product yield of batch synthesis.

As indicated, the environmental sustainability of flow synthesis could be improved by enhancing product yield. This underscores the importance of further research and development of flow reactors. It is suggested to explore alternative approaches for a more environmentally friendly process of HCP synthesis concurrently with the development of flow reactors. One key finding from both this and the previous LCA studies was that reagent consumption, especially DCE, is higher in flow synthesis for all three crosslinking approaches.

Overcoming this challenge could offer another pathway to reduce the environmental impacts of flow synthesis for all four endpoint impacts.



Assessing the environmental impacts of flow and batch syntheses of hypercrosslinked polymers for low-pressure CO₂ adsorption

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CO₂ adsorption

ABSTRACT

The microporosity of hypercrosslinked polymers (HCPs) renders such materials ideal adsorbents for carbon capture. We recently showed that the CO₂/N₂ selectivity of HCPs synthesised by internal crosslinking of poly- α,α' -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 CO₂ 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 CO₂/N₂ 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 (CO₂) 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 CO₂ emissions in the COP26 summit held in Glasgow in 2021. This commitment will affect the strategy for reducing and eliminating industrial-scale CO₂ emissions [1].

Utilising porous adsorbents for low pressure, physisorption of CO₂ 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 α,α' -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 CO₂ uptake [13]. The synthesis conditions, including synthesis duration and amount of crosslinker reagents, also had an impact on CO₂ 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 CO₂ and N₂ 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 cm³ g⁻¹ to 0.281 cm³ g⁻¹, whilst reducing pore widths from 2 to 6 nm to under 2 nm. Consequently, this enhanced CO₂/N₂ selectivity (calculated using ideal adsorption solution theory (IAST) with a mixture gas comprising CO₂ 85% and 15% N₂, at 298 K and 1 atm) by 850 %, reaching a value of 71 (Table 1). This steep increase in CO₂/N₂ 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 CO₂/N₂ 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 CO₂ adsorption is using a functional unit related to this process, *i.e.*, the amount of CO₂ 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 CO₂ uptake of modified activated carbon was higher by 2 mmol g⁻¹, 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 CO₂ adsorption (CO₂ 85% and 15% N₂ of inlet flue gas at 298 K and 1 atm). Fig. 1 shows the chemical structures of the

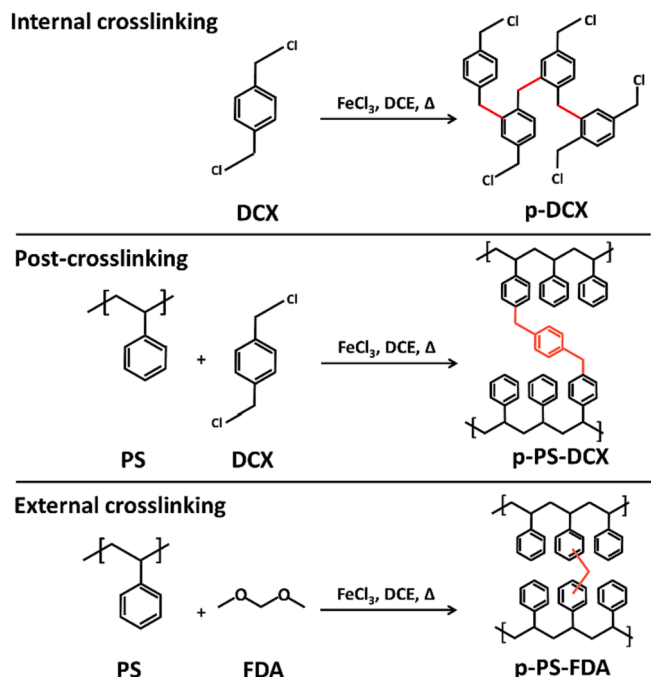


Fig. 1. Three synthetic crosslinking approaches for this LCA study.

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 CO₂ and N₂ adsorption and CO₂/N₂ 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 CO₂ 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 CO₂ 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 CO₂/N₂ 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 CO₂ from the inlet flue gas mixture of 15:85 M ratio of CO₂ and N₂ 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:

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

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 CO₂ adsorption stage was omitted from the system boundaries. The CO₂ 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 CO₂.

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 CO₂ 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 CO₂. 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 CO₂ 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).

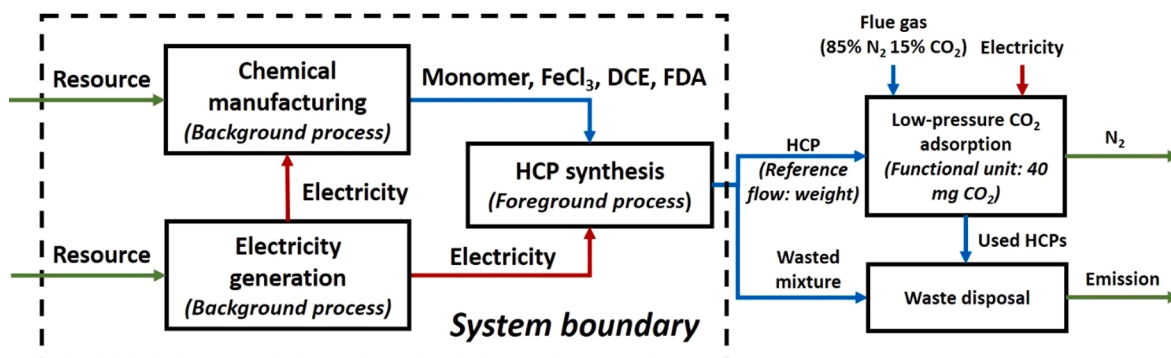


Fig. 2. System boundary of this LCA study as considered partial sections of the life-cycle of HCPs.

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
Input	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 ₃ (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
Output	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 CO₂ 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 CO₂/N₂ selectivity, increasing from 7.3 to 71.

3.2. The key for improving environmental impacts of CO₂ capture with HCPs from flow synthesis

From Fig. 3, it was clear that the CO₂/N₂ selectivity of HCP adsorbents was not key for reducing the environmental impacts of capturing 40 mg of CO₂ from a hypothetical 85:15 CO₂/N₂ mixture at 25 °C and 1 atm. This was because amongst all HCPs studied here, the CO₂/N₂ selectivity of internally crosslinked HCPs synthesised in flow reactions was the highest, reaching a value of 71 (Table 1). Meanwhile, the CO₂/N₂ selectivities of externally and post-crosslinked HCPs synthesised in flow reactions were 23 % and 25 % lower than those yielded from batch reactions. With lower CO₂/N₂ selectivities, 41 % and 55 % more post-

crosslinked and external crosslinked HCPs synthesised via flow reactions were required to capture 40 mg of CO₂. 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,

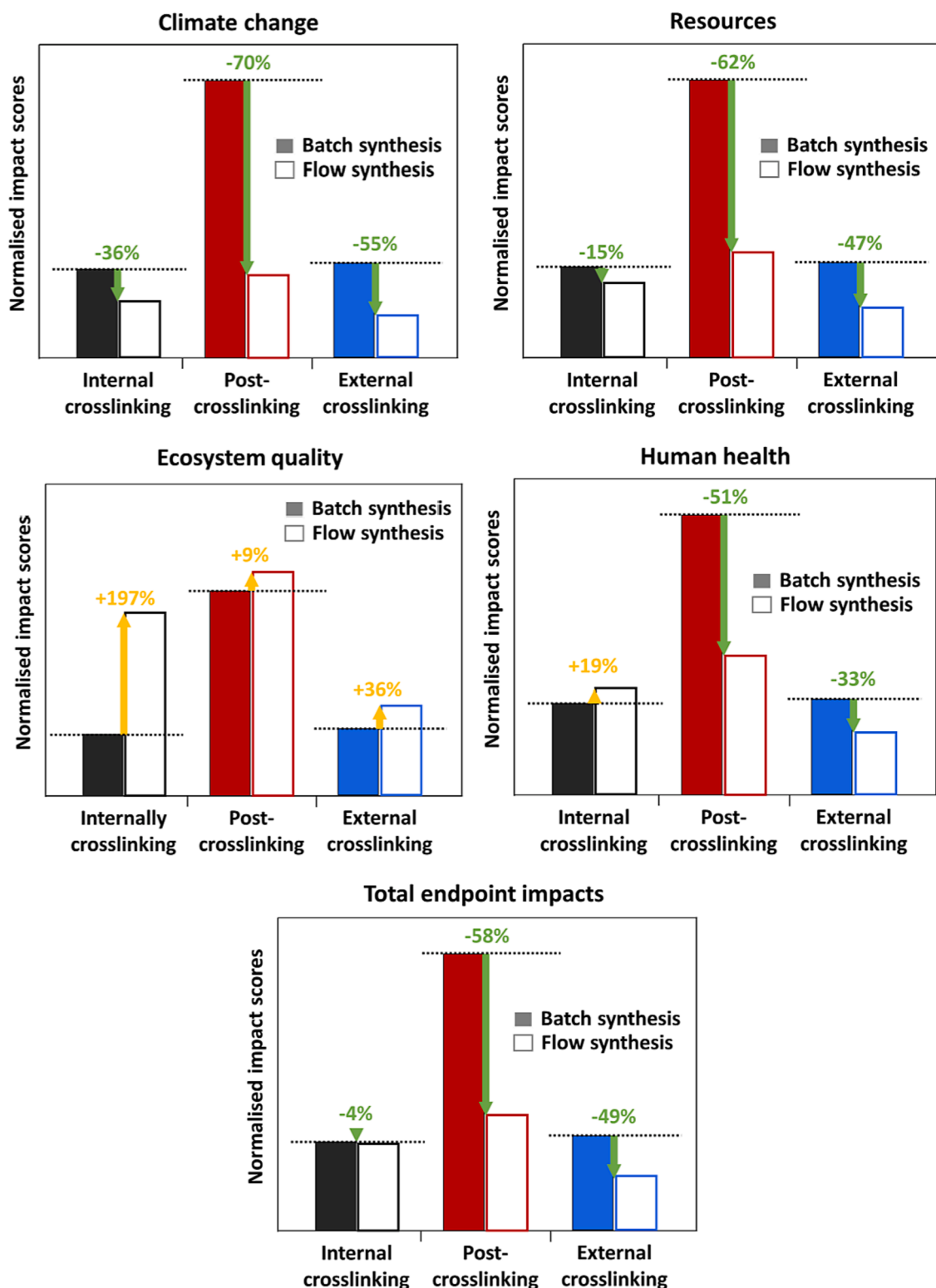


Fig. 3. Normalised endpoint impact scores for each synthesis process of three HCP types for capturing 40 mg CO₂ via low-pressure adsorption. The change in impact scores from batch synthesis to flow synthesis was highlighted with arrows for each synthetic approach.

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

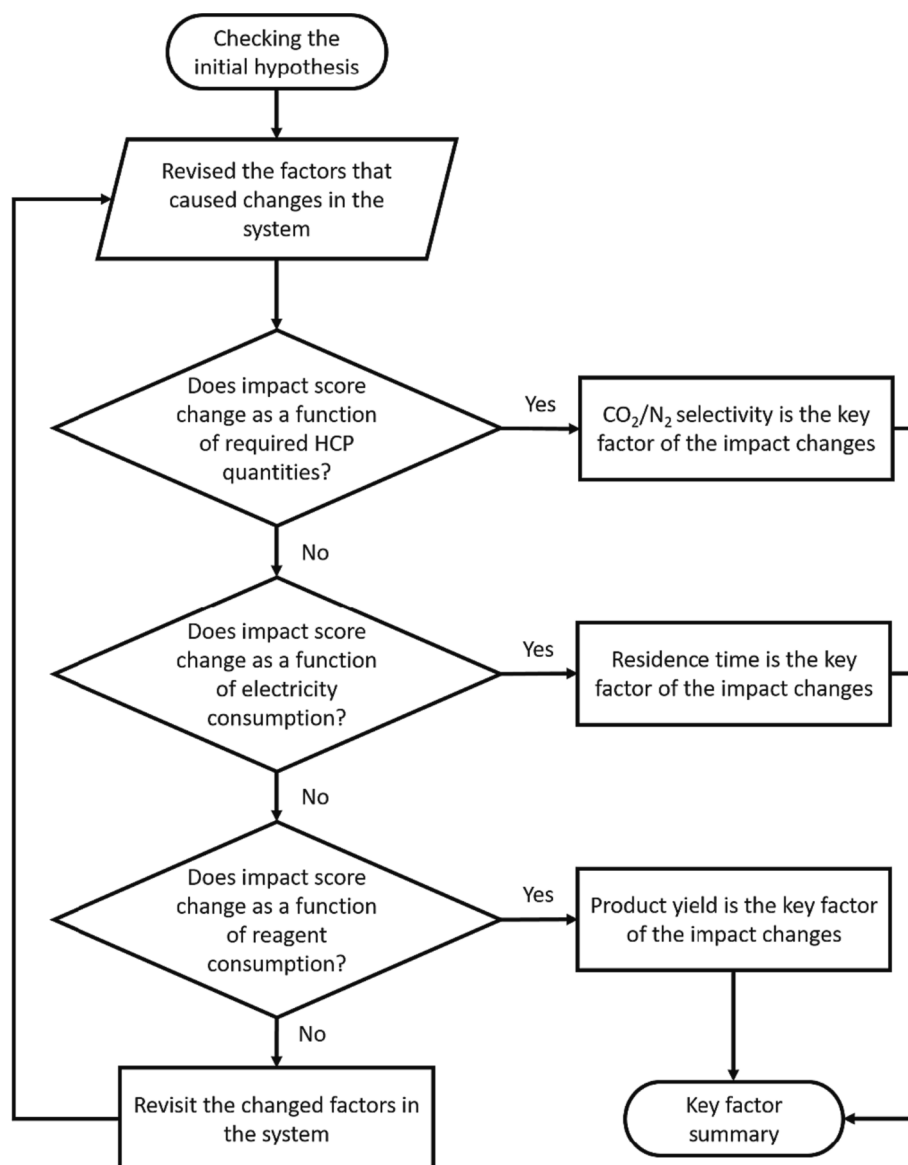


Fig. 4. The flowchart showing the thought process of which factor is the key of changing of impact scores.

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 CO₂ 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 CO₂ could reduce emissions of CO₂ 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 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 CO₂ 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 CO₂ 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_{2.5} 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 CO₂, flow synthesis of internal crosslinking would result in a 6 % higher of PM_{2.5} equivalent weight emitted, while flow synthesis of post- and external crosslinking would reduce the PM_{2.5} equivalent weight by 56 % and 39 %, respectively, when compared to batch synthesis (Figure S5). By identified 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 CO₂. 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 CO₂. 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

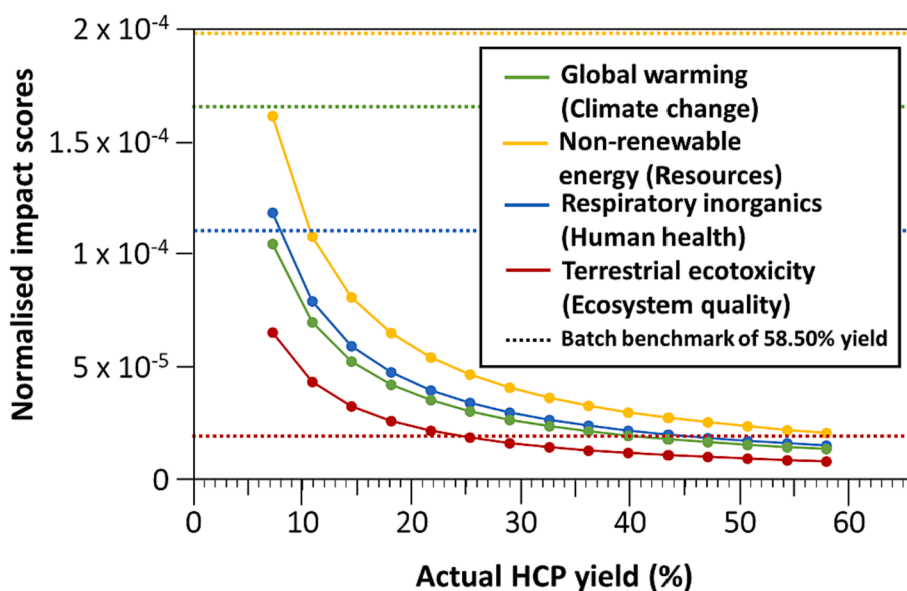


Fig. 5. Normalised impact scores of the synthesis process of p-DCX in flow system at different percent yields of flow-synthesised p-DCX. The solid lines represented the normalised impact scores of flow synthesis of internal crosslinking, while the dotted lines represented the impact scores of the batch 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 CO₂/N₂ selectivity in HCPs synthesised in flow synthesis would reduce environmental impacts by reducing the mass of HCPs required for capturing 40 mg of CO₂. 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 CO₂/N₂ selectivity. With advantages such as environmental impact reduction, high CO₂ 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 CO₂/H₂O selectivity of HCPs warrants attention, especially considering that that flue gas often comprises a similar weight percentage of H₂O steam as CO₂ [36,37], potentially leading to competition for adsorption sites. Competitive sorption between CO₂ and water has been observed in conditions, leading to lower CO₂ adsorption capacities in HCPs similar to the ones studies here [38]. Consequently, this could require a higher amount of HCPs for effective CO₂ 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 CO₂ adsorption after ten cycles [40]. This potential for recycling could substantially reduce the required amount of HCPs for CO₂ 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, CO₂ adsorption and CO₂/N₂ 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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Supplementary Information

Assessing the environmental impacts of flow and batch syntheses of hypercrosslinked polymers for low-pressure CO₂ adsorption

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Table S1 Foreground process inputs

Products / Services	Sources
Polystyrene, expandable {RER} production Alloc Def, U	Ecoinvent 3
P-dichlorobenzene {GLO} market for Alloc Def, U	Ecoinvent 3
Iron (III) chloride, without water, in 40% solution state {GLO} market for Alloc Def, U	Ecoinvent 3
Formaldehyde dimethyl acetal (FDA)	Created based on LCA literature ⁴¹
Ethylene dichloride {RER} production Alloc Def, U	Ecoinvent 3
Electricity, medium voltage {GB} market for Alloc Def, U	Ecoinvent 3

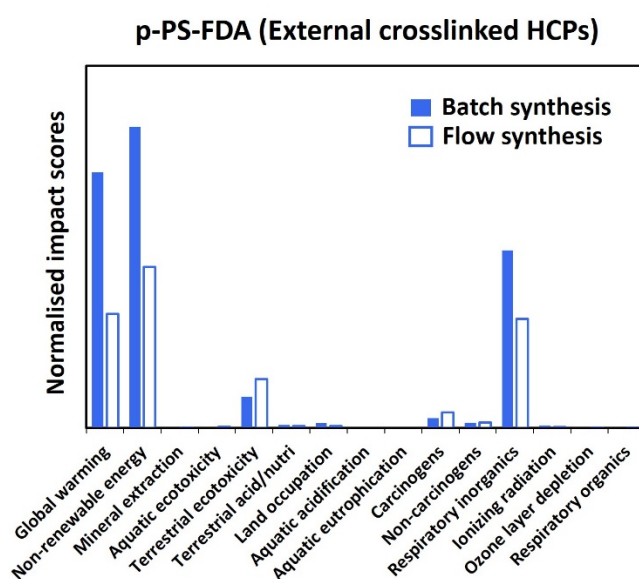
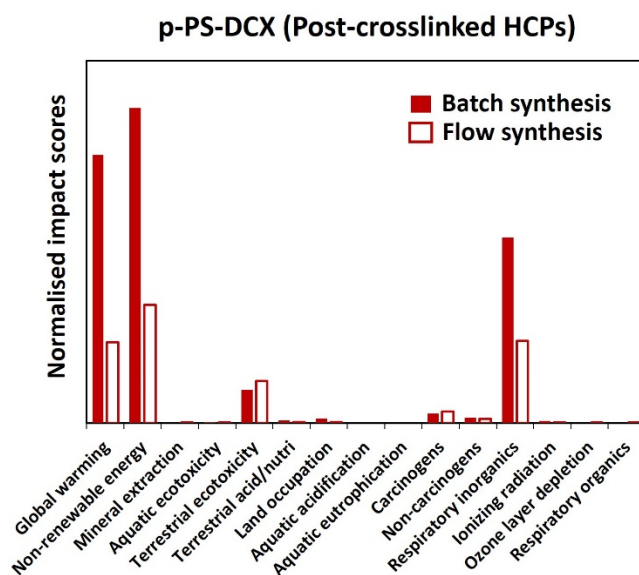
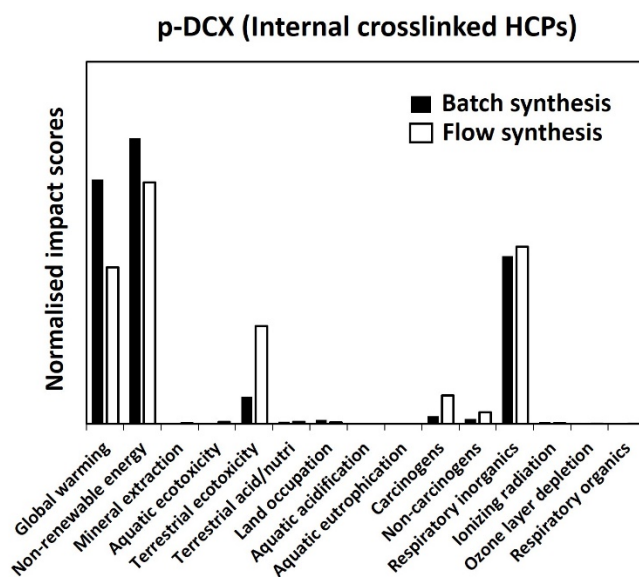


Figure S1 Normalised midpoint impact scores of the synthesis process of three HCP types for capturing 40 mg CO₂ via low-pressure adsorption

Midpoint impact under Climate change damage category

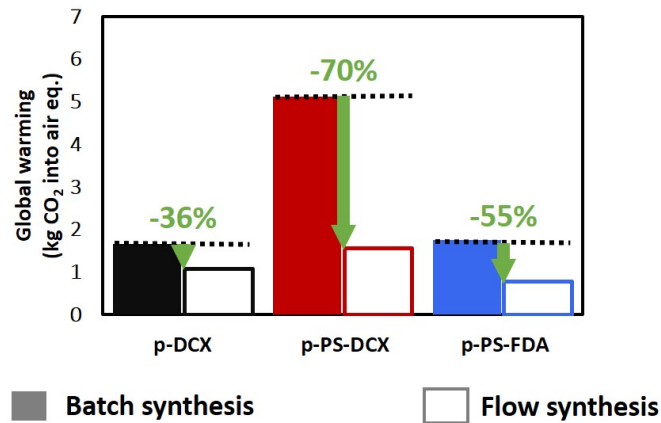


Figure S2 Midpoint impact category under Climate change damage category (Global warming) from the synthesis of three HCP types for 40 mg CO₂ capture via low-pressure adsorption. The changes of impacts after switching from batch to flow synthesis were presented in percentage.

Midpoint impacts under Resources damage category

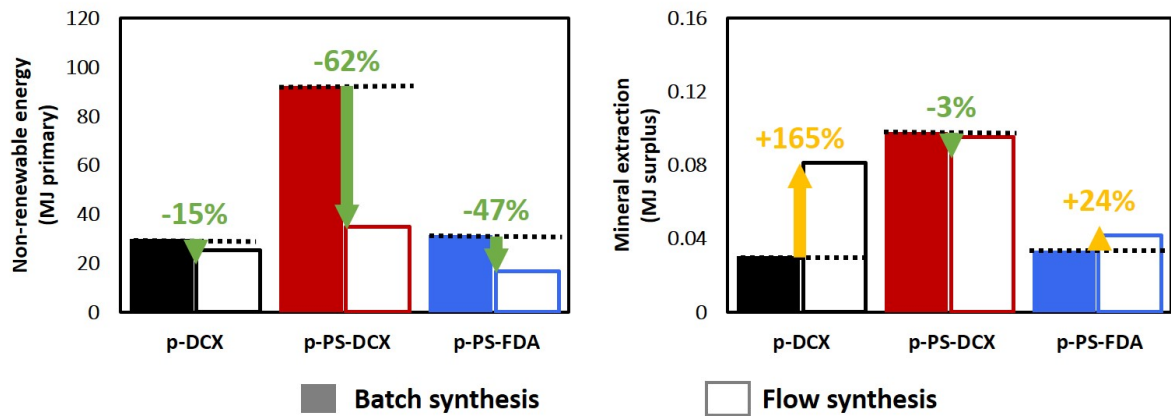


Figure S3 Midpoint impact categories under Resources damage category (Non-renewable energy; Mineral extraction) from the synthesis of three HCP types for 40 mg CO₂ capture via low-pressure adsorption. The changes of impacts after switching from batch to flow synthesis were presented in percentage.

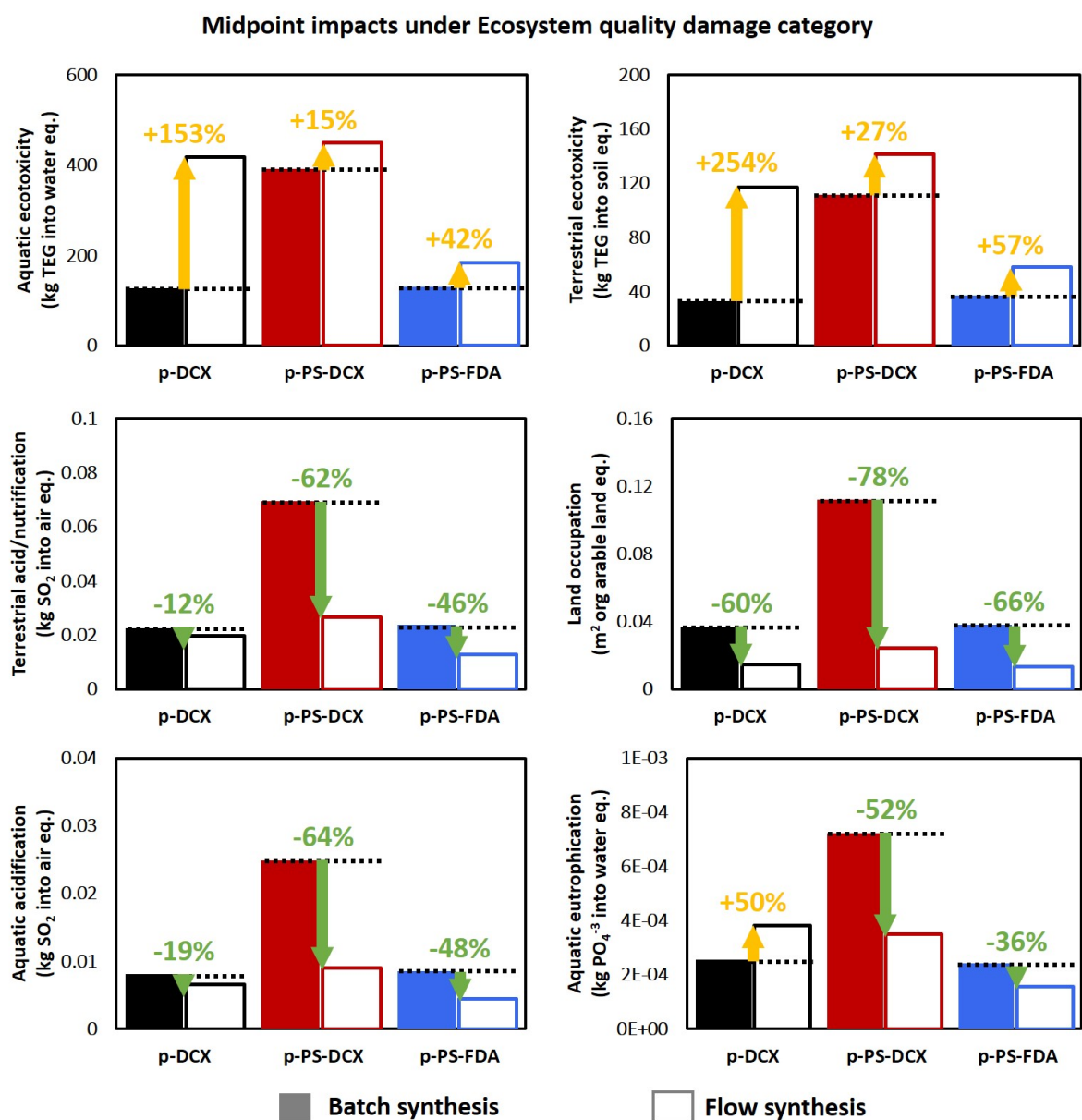


Figure S4 Midpoint impact categories under Ecosystem quality damage category (Aquatic ecotoxicity; Terrestrial ecotoxicity; Terrestrial acidification/nutrifaction; Land occupation; Aquatic acidification; Aquatic eutrophication) from the synthesis of three HCP types for 40 mg CO₂ capture via low-pressure adsorption. The changes of impacts after switching from batch to flow synthesis were presented in percentage.

Midpoint impacts under Human health damage category

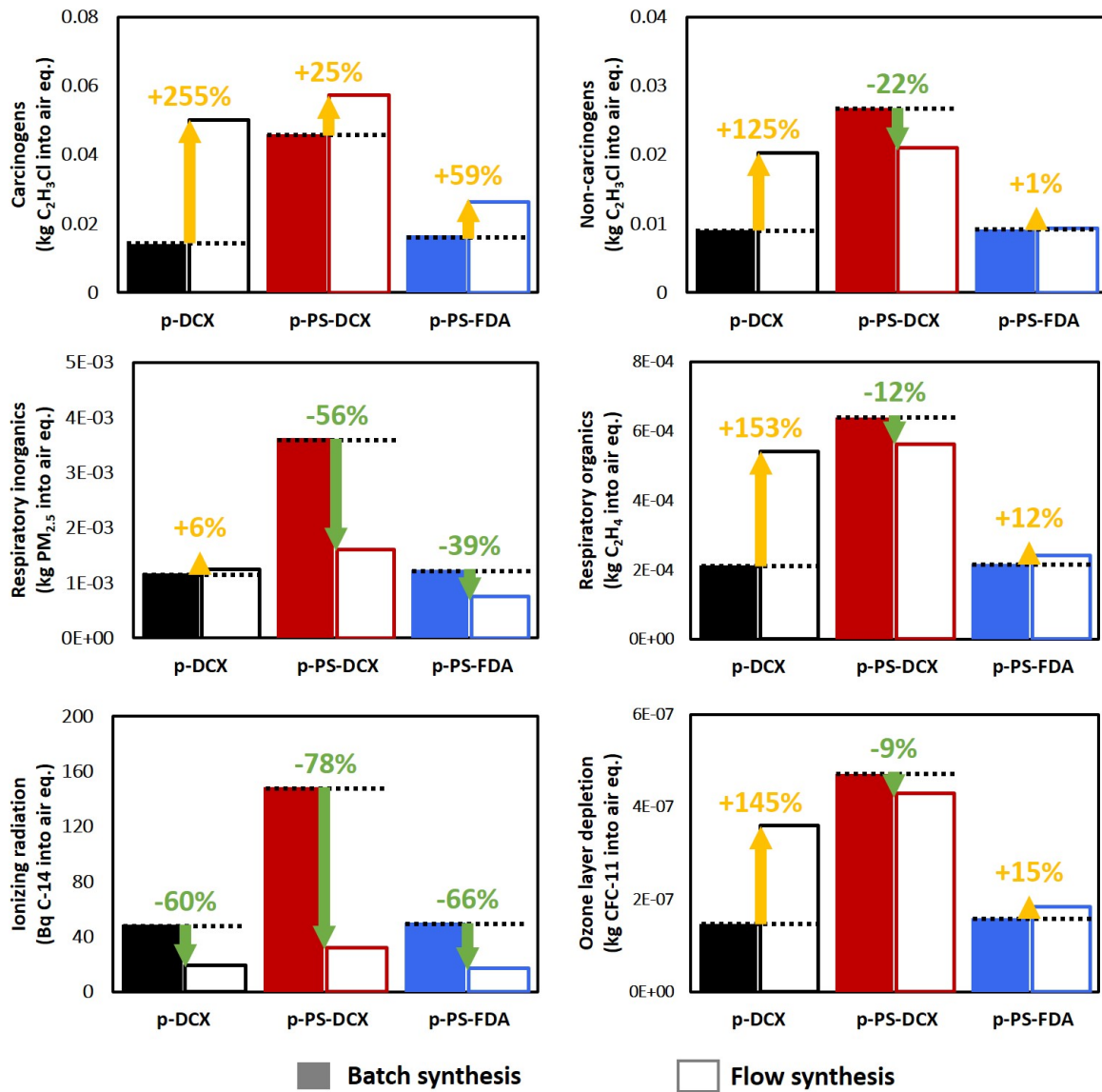
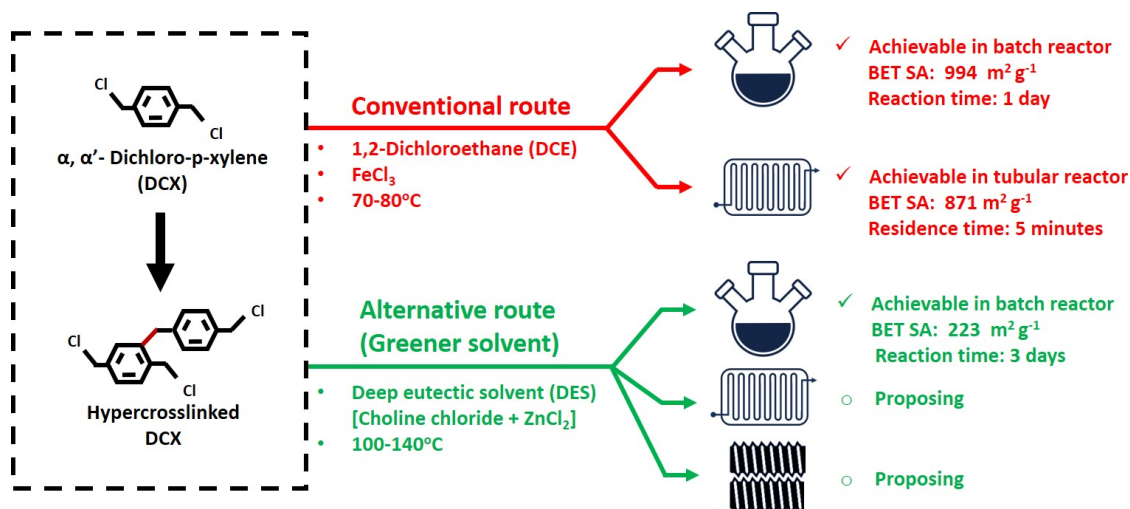


Figure S5 Midpoint impact categories under Human health damage category (Carcinogens; Non-carcinogens; Respiratory inorganics; Respiratory organics; Ionizing radiation; Ozone layer depletion) from the synthesis of three HCP types for 40 mg CO₂ capture via low-pressure adsorption. The changes of impacts after switching from batch to flow synthesis were presented in percentage.

Table S2 Inventory table for the sensitivity analysis

Increment	% HCP yield	Input for 1.055 g flow-synthesised p-DCX			
		DCX (g)	FeCl ₃ (g)	DCE (g)	Electricity (kWh)
0%	7.3	14.6	13.5	631.8	0.20
50%	10.9	9.7	9.0	421.2	0.13
100%	14.5	7.3	6.8	315.9	0.12
150%	18.1	5.8	5.4	252.7	0.09
200%	21.7	4.9	4.5	210.6	0.07
250%	25.3	4.2	3.9	180.5	0.06
300%	29.0	3.6	3.4	157.9	0.06
350%	32.6	3.2	3.0	140.4	0.05
400%	36.2	2.9	2.7	126.3	0.05
450%	39.8	2.7	2.5	114.8	0.04
500%	43.4	2.4	2.3	105.3	0.04
550%	47.1	2.2	2.1	97.20	0.04
600%	50.7	2.1	1.9	90.26	0.04
650%	54.3	1.9	1.8	84.24	0.04
700%	57.9	1.8	1.7	78.98	0.03

6. Continuous synthesis of HCP using DES as benign alternative



Graphical abstract - Proposed outline of the continuous HCP synthesis using DES as benign alternative

6.1. Introduction

In the field of HCP synthesis, many publications favoured using DCE as the reacting solvent due to its compatibility with the Friedel-Crafts alkylation.³ It was regarded as a thermodynamically good solvent, assessing *via* Hildebrand and Hansen solubility parameters.¹⁵ However, it has been categorised as highly hazardous and “undesirable/major issues” according to the CHEM21 selection guide⁹⁷ and medical chemists,⁹⁶ respectively. This reputation is mainly attributed to its carcinogenic properties⁹⁷ and the chlorine content, which transformed into non-recycled halogenated waste by the end of the synthesis process.

In response to the environmental concern surrounding these hazardous solvents, various efforts have been made to find more environmentally friendly alternatives. One such substitute, employed for Friedel-Crafts reactions, is the deep eutectic solvent (DES).⁹⁹ It is classified as an ionic liquid and typically consists of two components: ChCl and chloride anion. My research group also ventured into employ DES for HCP synthesis *via* Friedel-Crafts alkylations.¹²⁴ This endeavor resulted in the creation of hypercrosslinked DCX with a BET surface area of $400 \text{ m}^2 \text{ g}^{-1}$, achieving after a 72-hour reaction period using $[\text{ChCl}][\text{ZnCl}_2]_2$. Furthermore, external crosslinking of triptycene with FDA crosslinker in $[\text{ChCl}][\text{FeCl}_3]_2$ was achieved within 24 hours, yielding a BET surface area of $970 \text{ m}^2 \text{ g}^{-1}$. These findings underscore the potential of DES as a more benign solvent alternative to conventional DCE.

Building on the success of batch synthesis using DES as a more benign alternative, this work proposed the transition of HCP synthesis using DES from batch to a continuous flow system. This proposition aimed to harness the advantages of flow synthesis, primarily its reduced reaction time leading to lower energy consumption. By incorporating a more benign solvent like DES, the generation of fewer hazardous waste byproducts was anticipated, ultimately, the continuous flow synthesis of HCPs using DES promising a higher level of process sustainability than previously achievable.

6.2. Continuous flow HCP synthesis using DES as benign alternative

The combination of upscaling HCP synthesis using DES as an alternative solvent had not been previously reported. One challenge that potentially hindered the continuous flow process was that the DES mixture only remains fluid at a specific temperature.¹²⁵ Unlike solid substrates that are typically soluble in DCE solvent, the fluidity of DES could be compromised when not adequately heated during transport through the tubing. To overcome this issue, a seamless connection between the feeding system and the reaction area, coupled with a continuous heating system, became imperative. Therefore, this unconventional approach necessitated a new synthetic method rather relying on a conventional continuous flow reactor.

6.2.1. Experimental procedure

The continuous flow system underwent reconstruction for this experiment (Figure 1). The primary modification in this version of the flow system involved the incorporation of a heating medium within the feed storage equipment. The majority of the syringe pump was 3D printed to accommodate this additional feature. Acrylonitrile butadiene styrene was chosen as the material for the part in close contact with the heater due to its higher melting point, while polylactic acid was employed for other parts subjected to more mechanical stresses. A 10 mL or 20 mL glass syringe was utilized as a mini-feed storage container containing a pre-mixed room temperature solid DCX, CHCl_3 , and ZnCl_2 mixture. A silicon heater mat (RS PRO Silicone Heater Mat, 1.25 W, 25 x 50 mm, 12 V DC), connected to the temperature controller, was wrapped around the glass syringe, as depicted in Figure 2. A thermistor was positioned under the wrap to monitor the real-time temperature of the syringe. Insulation fiberglass was interposed between the heater mat and the 3D printing part. The glass syringe, enveloped by the heater mat and insulator, was secured with the 3D printing part, as shown in Figure 3.

The flow system was driven by a motor connected to a controller. The flow rate was set as a default to 1 mL min^{-1} . The syringe was connected to a straight 20 cm, 2 mm inner diameter PTFE tube. The majority of the tube's length was placed directly on the hot plate. The setup allowed only a small gap connecting the syringe and the tube to remain unheated, ensuring uniform heating throughout the system.

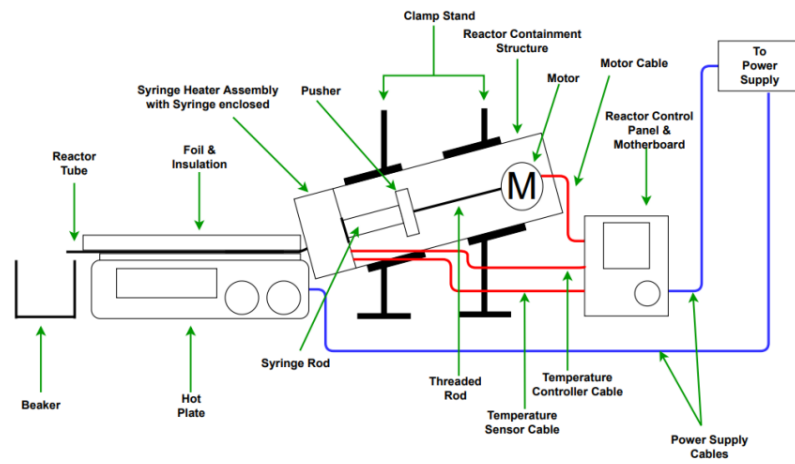


Figure 1 The continuous flow system coupled with a heating system for feed storage (Image produced by K. Kapur)

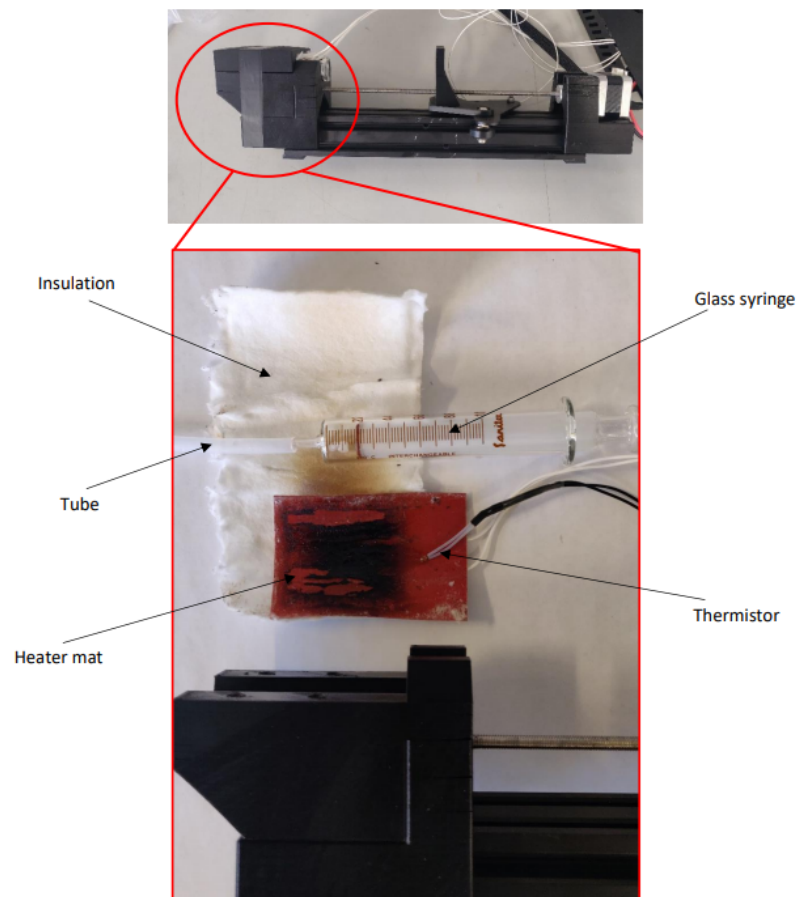


Figure 2 The unwrapped heating equipment of the continuous flow system (Image from N. Rog)

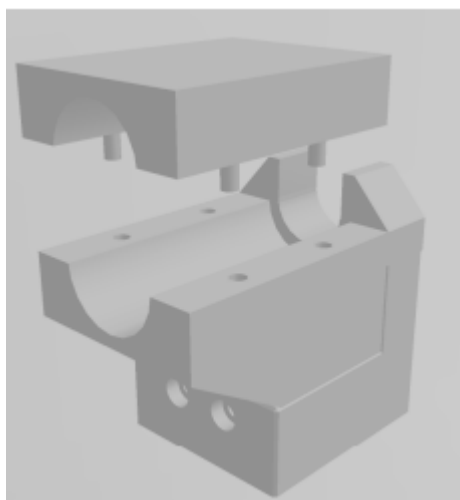


Figure 3 3D model of the syringe holder (Image produced by N. Rog)

This experiment focused on the internal crosslinking of DCX to serve as a benchmark against batch synthesis. The batch synthesis protocol was carried as following. The molar ratio of the DES composed of ChCl and ZnCl_2 was 1:2, and the molar ratio of DCX to ZnCl_2 was 1:28. The operation was conducted at a constant temperature of 100 °C with continuous mixing for 72 hours. The preliminary test of flow synthesis followed the exact batch synthesis protocol, except for the reaction time, which adhered to the feed flow rate. The adjustment of operating parameters, including syringe temperature, hotplate temperature, and the molar ratio of DCX to ZnCl_2 , was investigated in the latter part of the experiment. At the end of each experiment, the slurry product was collected from the end of the reactor tube. The product was dissolved in excess DI water to reduce the viscosity of DES and then filtered using a Buchner flask, a funnel, and a vacuum pump to separate the solid HCP particles. The obtained HCPs were dried in an oven at 120 °C overnight.

The synthesised HCPs using DES, both from batch and flow, were characterised for BET surface area and molecular structure using N_2 adsorption gas analyser and ^{13}C NMR spectroscopy, respectively. The residence and reaction times were recorded for the STY calculations to compare the productivity of both methods.

6.2.2. Results and Discussions

During the preliminary experiment, the new setup of the continuous flow system for HCP synthesis using DES as solvent demonstrated non-uniform heating across the cross-section of the glass syringe. Solid dark red particles were observed forming on the inner wall surface of the glass syringe. This indicated that the heat transferred from the heater mat to the syringe's wall could initiate the pre-crosslinking of the feed stored inside the syringe. Simultaneously, the feed mixture located near the core of the barrel received enough heat to become fluid and was ejected from the syringe into the reactor tube. In this case, the syringe itself could be treated as semi-batch reactor.

Within the semi-batch reactor, solid particles could be observed at temperature ranging from 100 – 120 °C within 5 minutes of pre-heating the syringe, a timeframe similar to the batch experiment, resulting in a product yield below 5 %. Conversely, at 180 °C within 5

minutes of pre-heating the syringe, dried solid product could be obtained from the syringe, yielding up to 34 %. This yield was lower than the batch product yield by 45 %, which reached 61 %. This product from semi-batch (p-DCX-DES/SB) underwent characterisation for molecular structure and BET surface area, alongside the HCP from batch synthesis using DES as solvent (p-DCX-DES/B). Both HCPs from batch and semi-batch synthesis exhibited similar molecular structures, as shown in Figure 4. The major peak of 37 ppm indicated the presence of carbon from crosslinked bridges, confirming that the product from semi-batch synthesis was the same species of HCP as the product from batch synthesis. The BET surface area of the semi-batch-synthesised HCP was $213 \text{ m}^2 \text{ g}^{-1}$, which was 4 % lower than the BET surface area of batch-synthesised HCP, which was $223 \text{ m}^2 \text{ g}^{-1}$. This finding indicated that the synthesis of HCP using DES as a solvent could be achieved in a semi-batch process with a similar textural quality to the HCP from batch synthesis but in a shorter time, reducing it by 99 % from 3 days to 5 minutes. It is possible that this difference resulted from the smaller surface area-to-volume ratio of the glass syringe compared to the rounded flask. However, the main goal of achieving HCP synthesis using DES as an alternative solvent *via* continuous flow had not yet been fully accomplished.

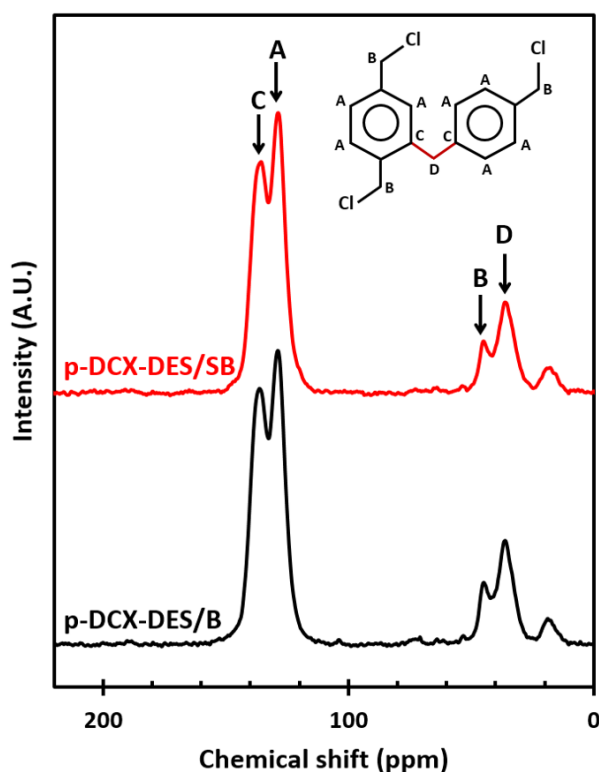


Figure 4 ^{13}C NMR spectra of p-DCX-DES/B and p-DCX-DES/SB

In order to consider obtaining flow-synthesised HCPs using DES as the solvent, it was imperative to collect them in the form of slurry product at the end of the reactor tube. Solid particles forming inside the syringe barrel were categorised as products from the semi-batch synthesis, as previously done in the preliminary experiment. To mitigate the rapid formation of solid product inside the syringe barrel, a series of adjustments to three operating parameters, consisting of syringe temperature, heating plate temperature, and molar ratio of DCX to ZnCl_2 , were conducted within the same continuous flow reactor setup. The syringe

temperature was lowered to a range of 100 – 140 °C, to decelerate the pre-crosslinking stage within the glass syringe barrel. The hotplate temperature was maintained between 170 – 210 °C. Furthermore, the molar ratio of DCX to ZnCl₂ was altered, opting for a new ratio of 1:43 over the original 1:28. The new ratio was grounded in the hypothesis that a higher amount of catalyst might accelerate the crosslinking reaction, while a lower DCX amount could help prevent reactor clogging due to the solidification of HCP product. The molecular structure of the products from continuous flow synthesis (p-DCX-DES/F) and the semi-batch synthesis (p-DCX-DES/SB) under the same operation (140 °C syringe temperature, 210 °C hotplate temperature, and 1:43 molar ratio of DCX:ZnCl₂), which yielded the highest flow-synthesised product, was identified by ¹³C NMR spectroscopy (Figure 5). The presence of a peak at 34 ppm in both spectra provide confirmation of the existence of crosslink network, indicating that both product samples were HCPs. With HCPs confirmed, further investigation into the influence of operating parameters on product yield and BET surface area was undertaken.

The trends in product yield influenced by each parameter are depicted in Figure 6. Overall, the product yield at a molar ratio of DCX to ZnCl₂ of 1:43 was averagely 1.6 % higher compared to the product yield at a molar ratio of 1:28. This observation, along with the 1.5 fold molar increment of ZnCl₂ per mole of ChCl, contrasted with previous research on HPC synthesis using DES in batch. In that context, an increase in the catalyst amount per mole of monomer, specifically raising the ZnCl₂ from 8 to 50 mole per mole of DCX, resulted in an increase in BET surface area from 6 to 477 m² g⁻¹.¹²⁴ This suggests that the quantity of ZnCl₂ used may not justify the obtained HCP product yield in this continuous flow reactor design. Regarding syringe temperature, the product yield percentage increased by an average of 2, when the temperature from 100 °C to 120 °C. However, when the temperature increased to 140 °C, the product yield percentages of the flow-synthesised HCPs either remained the same or decreased. This suggests that the optimal syringe temperature of 120 °C induced pre-crosslinking at a level that did not clog the system. Conversely, the product yield increased with the increment of the hotplate temperature, indicating that higher temperatures provided more heat to the tube reactor, enhancing the kinetic rate of crosslinking reaction. The maximum yield of HCP from flow synthesis, among all parameter adjustments, was approximately 12 %. This finding implies that the majority of the crosslinking reaction still occurred inside the glass syringe barrel, regardless of the operating parameter adjustment. Furthermore, agglomeration of crosslinked product was observed on the inner wall surface of the tube reactor, likely due to the high viscosity of DES. The force from driven flow was unable to overcome the resistance of interfacial interaction between the agglomerated product and the tube wall. With a fixed feed flow rate of 1 mL min⁻¹, a tube with a 2 mm inner diameter, and a length of 20 cm, the average residence time for all tests was 10 minutes. This resulted in a STY of 1727 mg mL⁻¹ day⁻¹ for the test that yielded the highest product, under the conditions of 140 °C syringe temperature, 210 °C hotplate temperature, and a 1:43 molar ratio of DCX:ZnCl₂. This STY outperformed HCP batch synthesis using DES as a solvent and HCP continuous flow synthesis using DCE as a solvent by 86 and 3 fold, respectively.

Regarding BET surface area, the highest specific surface area among HCPs from continuous flow synthesis was 56 m² g⁻¹, obtaining under the conditions of 140 °C syringe

temperature, 170 °C hotplate temperature, and a 1:43 molar ratio of DCX to ZnCl_2 . This BET surface area was 75 % lowered than that of the HCP from batch synthesis using DES as an alternative solvent, in stark contrast to the 1.5 % difference in BET surface area between batch and continuous flow synthesis of HCP *via* conventional route. This difference may be attributed to the poor heat and mass transfer within the system. Due to the higher viscosity of DES compared to DCE, the flow pattern in the straight tube exhibited laminar flow behaviour instead of turbulent flow. This was evident from the observation that chunks of dark red crosslinked particles travelled at velocity less than 1 cm min^{-1} . Taking this finding into account, along with the fact that batch synthesis involved lower operating temperature and the molar ratio of ZnCl_2 , which were at 100 °C and 1:28, respectively, it becomes apparent that the current apparatus for continuous flow HCP synthesis using DES may not be as well-suited for upscaling as demonstrated in continuous flow HCP synthesis using DCE, unless further system improvements are taken into considerations.

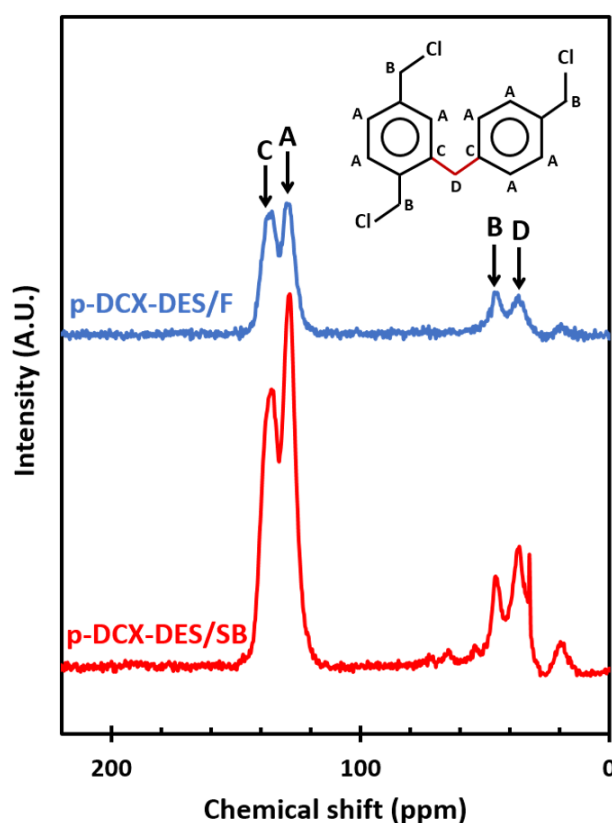


Figure 5 ^{13}C NMR spectra of p-DCX-DES/SB and p-DCX-DES/F from 140 °C syringe temperature, 210 °C hotplate temperature, and 1:43 molar ratio of DCX: ZnCl_2

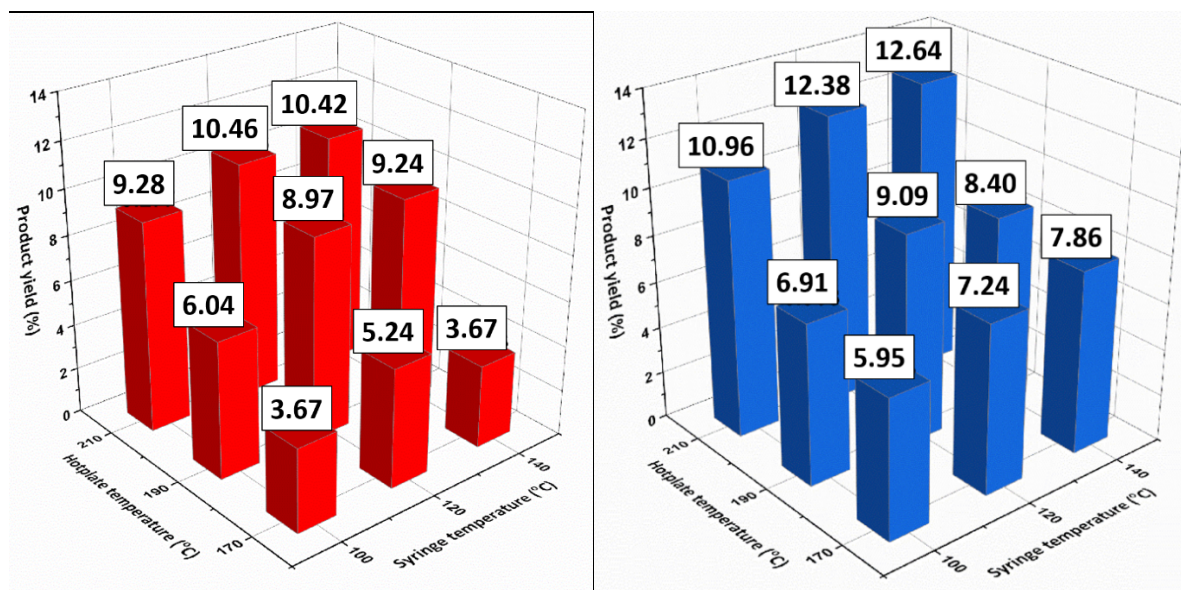


Figure 6 Percent product yields of HCPs from flow synthesis at different operating parameter conditions. The red and blue bars represented HCP from the molar ratio of DCX:ZnCl₂ of 1:28 and 1:43, respectively.

6.2.3. Conclusions and limitations

In conclusion, this newly design continuous flow system had demonstrated the failure for HCP synthesis using DES as a more benign alternative, thereby showcasing the infeasibility of transitioning HCP synthesis using DES as a solvent from a batch to a continuous flow system. It has revealed four significant issues that required further development. Firstly, it is crucial that the feed mixture is not exposed to a heat source during storage; it should be heated instantly before being fed into the reactor. This precaution helps prevent clogging caused by pre-crosslinking outside the reactor, which leads to low product yields during continuous flow synthesis. Secondly, ventilation must be incorporated into the system because hydrogen chloride is a by-product of the Friedel-Crafts alkylation of DCX. As a glass syringe is used as the feeding equipment, the accumulation of hydrogen chloride gas could pose a safety risk by potentially shattering the glass. Thirdly, in this experiment, the reactor tube was not uniformly heated as it was directly placed on the hotplate surface. Despite the presence of a fiberglass insulator covering on top of the tube, it was observed that colour changes due to the crosslinking process occurred more on the bottom side where the heat directly contacted the tube. Moreover, the hotplate surface was not evenly heated, with the highest temperature, according to the infrared thermometer, at the centre point gradually decreasing further away from the centre. Fourthly, the lack of mixing inside the reactor tube resulted in poor heat and mass transfer, subsequently leading to a low crosslinking rate and, consequently, a low BET surface area of HCPs. While continuous flow synthesis of HCP using DES as a more benign alternative offers advantages in terms of productivity compared to batch synthesis using DES, these aforementioned shortcomings still hinder the implementation of the continuous flow system for large-scale manufacturing of HCP synthesis process.

6.3. Continuous mechanochemistry for HCP synthesis using DES as benign alternative

Given the identified shortcomings of the new continuous flow setup for HCP synthesis using DES, particularly concerning the handling of DES within the system, the introduction of TSE emerged as an ideal solution. This approach allows for the separate storage of reagents in individual input feeding funnels, simplifying chemical management. The reagents are automatically mixed and transported through the rotation of the twin screw, reducing the need for manual labour in the process. With the barrel equipped with a heating controller, high-temperature reactions can be conducted through the TSE. Furthermore, the rotational force of the twin screw can transport viscous fluid using mechanical force, mitigating clogging issues. Consequently, TSE has become a prime candidate for the synthesis of HCP using DES as a more benign alternative, where solid components forming DES can be liquefied, mixed with substrates, and easily transported along the barrel.

The initial proposal for this work involved the synthesis of p-DCX using DES derived from ChCl and ZnCl_2 , the same system as the previous batch and semi-batch research. It was established that mixing of ChCl and ZnCl_2 would not corrode the stainless-steel extruder, as the synthesis of this type of DES had been successfully performed *via* TSE.¹²⁶ However, it had been realised that the stainless steel extruder could be corroded by hydrogen chloride, a by-product of the reaction. To circumvent the production of hydrogen chloride, benzyl alcohol (BA), a monomer containing a hydroxyl group, was selected, as it produces H_2O steam as a by-product. This not only ensures the safety of the extruder but also aligns with environmental considerations. BA has been reported to polymerise successfully through Friedel-Crafts alkylation in batch process using conventional DCE solvent.^{29, 38} Additionally, 1,3,5-triphenylbenzene (TPB) was chosen as a monomer, producing methyl alcohol as a by-product *via* Friedel-Crafts alkylation in an external crosslinking approach.⁴¹ The synthesis of these monomers using DES in batch through external crosslinking approach has been achieved within my research group. In this context, p-BA and p-TPB synthesised from DES exhibited BET surface areas of 352 and 384 $\text{m}^2 \text{g}^{-1}$, respectively,¹²⁴ though these values were lower by 34 % and 75 %, respectively, than those synthesised from DCE. This difference may be attributed to the reduced reactivity of ZnCl_2 as a catalyst when compared to FeCl_3 , which is used in the conventional route synthesis. Consequently, this study investigated the continuous mechanosynthesis of HCPs from BA and TPB using $[\text{ChCl}][\text{ZnCl}_2]_2$ (an abbreviation of DES composed of a 1:2 molar ratio of ChCl to ZnCl_2) *via* TSE, with the incorporation of FDA achieve the external crosslinking approach.

6.3.1. Experimental procedure

A lab-scale TSE was utilised for the HCP synthesis using DES, as shown in Figure 7. The co-rotating twin screw had the configuration depicted in Figure 8, with conveying sections and kneading sections arranged alternately. Encased within the extruder barrel, the screws were divided into six individual heating sections (Figure 9). The feeding port was located at the first heating section on the left-hand side, and the final product exited through the sixth section on the right-hand side. Temperature control for each section and screw rotating speed

adjustment were managed *via* the control panel shown in Figure 10, with all six heating sections set to a temperature of 180 °C. The screw speed was maintained at the lowest setting, which was 15 rpm, to prolong the reaction residence time.

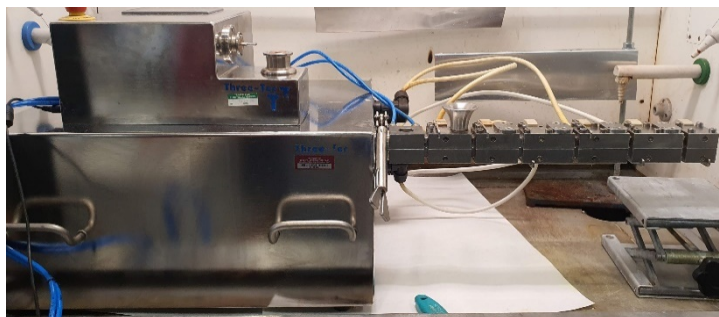


Figure 7 Twin screw extruder



Figure 8 Interior of the extruder barrel, showing the co-rotating screw and its configuration

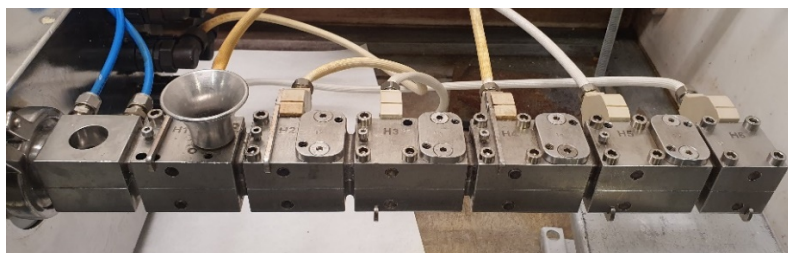


Figure 9 Exterior of the extruder barrel

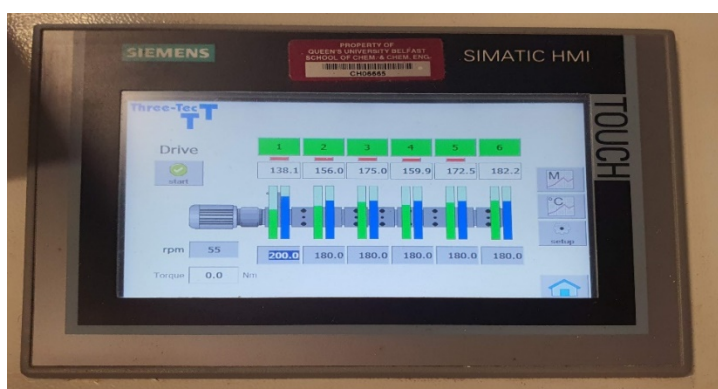


Figure 10 Temperature and screw speed control panel

The synthesis of p-BA using $[\text{ChCl}][\text{ZnCl}_2]_2$ *via* TSE proceeded as follows. The feed mixture of BA, ChCl, and ZnCl_2 was hand-mixed in a glass beaker in a molar ratio of 1:4:8 (3.00 g BA, 15.49 g ChCl, and 30.25 g ZnCl_2). This mixture was then fed into the extruder through the feeding port. After approximately 5 minutes, a viscous fluid was obtained at the end of the

barrel. This fluid was subsequently re-fed into the same extruder, a step repeated four more times, for a total of five passes. During this process, a portion of the product mixture progressively darkens with each pass, while another part remained transparent. The dark brownish compound and the clear fluid in the mixture were assumed to be lightly crosslinked BA and liquefied $[\text{ChCl}][\text{ZnCl}_2]_2$, respectively (Figure 11). On the sixth pass, 5 mL of FDA was added to the re-fed mixture, and this step was repeated thrice, resulting in a total consumption of 15 mL or 13 g, equivalent to 6 moles of FDA. The product mixture turned completely dark by the sixth pass, indicating the on-going reaction (Figure 11). By the eighth pass, the total operating time was approximately 1 hour. The final product mixture was retrieved, mixed with an excess volume of DI water until DES was dissolved, resulting in a less viscous mixture. This mixture was then filtered and washed with methanol. A heap of solid particles was transferred to a petri dish, covered with aluminum foil, and dried in an oven overnight.

The same procedure was applied to the synthesis of p-TPB using DES *via* TSE. The feed mixture consisted of TPB, ChCl, and ZnCl_2 in the molar ratio of 1:4:8 (3.00 g TPB, 5.47 g ChCl, and 10.68 g ZnCl_2). The re-feeding stage, addition of FDA, and retrieval of solid products followed the exact step used in the synthesis of p-BA. Regardless of the feeding cycle, the colour of the product mixture and the dried solid particles of p-TPB remained white, similar to unreacted TPB (Figure 12). The synthesised products were stored in a glass vial for ^{13}C NMR spectroscopy and N_2 adsorption at 77 K characterisation to determine molecular structure and BET surface area, respectively.



Figure 11 Colour of the product mixture for p-BA synthesis after fed into TSE after 5 passes (Left) and 8 passes (Right)



Figure 12 Colour of the product mixture for p-TPB synthesis after fed into TSE after 8 passes (Left) and colour of dried solid product (Right)

6.3.2. Results and Discussions

The solid particles, expected to be HCP products, were labelled as p-BA-DES/TSE and p-TPB-DES/TSE. The ^{13}C NMR spectra of these samples were compared with the corresponding HCP species synthesised *via* batch synthesis using DCE and $[\text{ChCl}][\text{ZnCl}_2]_2$ as the solvent, as shown in Figure 13. In the ^{13}C NMR spectra of p-BAs, all three spectra exhibited three significant peaks corresponding to different carbon locations denoting by alphabets. A peak near 40 ppm was assigned to the methylene carbon at location B,³⁸ confirming the presence of crosslinking bridges resulting from Friedel–Crafts alkylations. The absence of a peak at 65 ppm representing the carbon in the $-\text{CH}_2\text{OH}$ group (location D)¹²⁷ indicated that the crosslinking also occurred *via* the hydroxyl group.²⁹ The eliminated $-\text{OH}$ was transformed into a by-product H_2O molecule, which was considered a safe compound when in contact with the stainless-steel extruder. This suggests that crosslinking occurred during the synthesis of p-BA using $[\text{ChCl}][\text{ZnCl}_2]_2$ *via* TSE. Conversely, the ^{13}C NMR spectra of p-TPBs differed among all three samples. A peak assigned to methylene carbon at 32 ppm (location B)^{12, 41} was absent from the spectra of p-TPB synthesised using $[\text{ChCl}][\text{ZnCl}_2]_2$ *via* TSE. This indicated that the synthesis of p-TPB using $[\text{ChCl}][\text{ZnCl}_2]_2$ *via* TSE was unsuccessful. However, in the spectra of p-TPB synthesised using $[\text{ChCl}][\text{ZnCl}_2]_2$ *via* batch, the merging of peaks at 128 and 136 ppm, commonly observed in HCP species, was evident, similar to the spectra of p-TPB synthesised using DCE *via* batch. Despite the unclear peak assigned to methylene carbon from crosslink bridges in the spectra of DES-synthesised HCP compared to the noticeable peak in the spectra of DCE-synthesised HCP, these findings could indicate that the synthesis of TPB using $[\text{ChCl}][\text{ZnCl}_2]_2$ as a solvent might be achievable but less favourable compared to using DCE as a solvent.

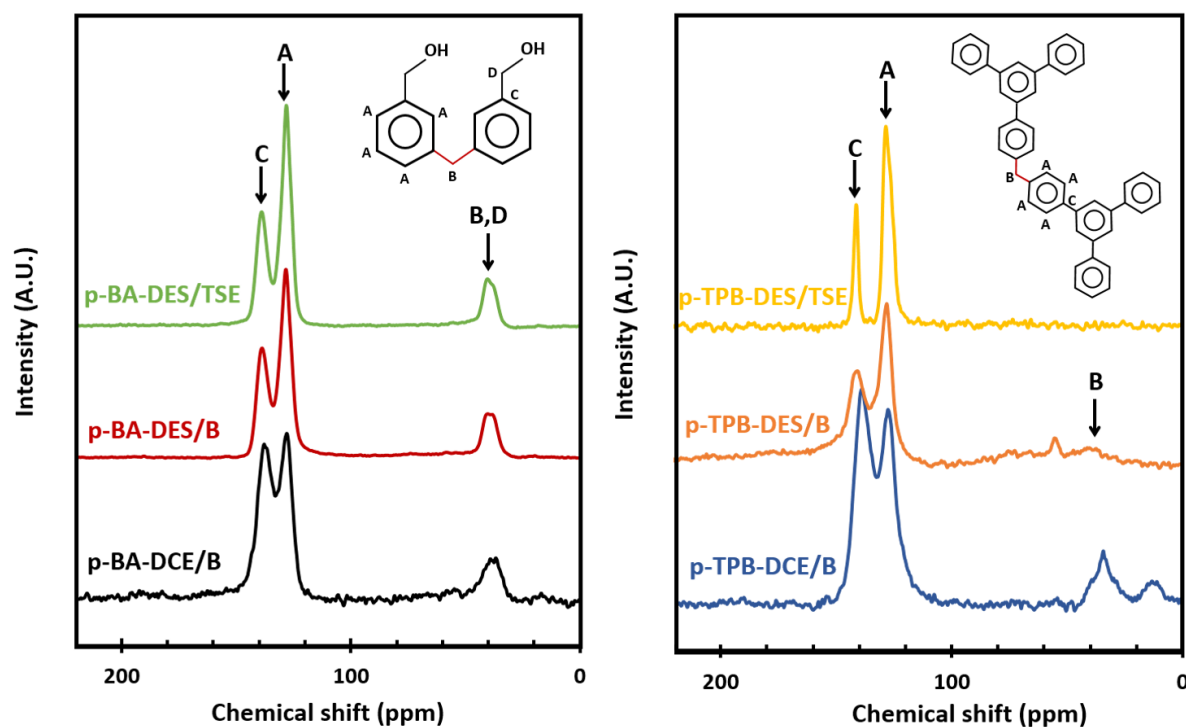


Figure 13 ^{13}C NMR spectra of p-BA (Left) and p-TPB (Right) from three synthesis approaches: Using DCE via batch synthesis, using DES via batch synthesis, and using DES via TSE

The N_2 adsorption isotherm at 77 K of p-BA-DES/TSE (Figure 14) showed a pattern characterised by positive gas adsorbed values at $P/P_0 < 0.2$, followed by negative values at P/P_0 ranging from 0.2 – 0.8, and then returned to positive values at $P/P_0 > 0.8$. This type of isotherm shape typically indicates a material that is either non-porous or has a low specific surface area,¹¹¹ which aligned with the measured BET surface area of $0.5387 \text{ m}^2 \text{ g}^{-1}$. This suggests that the crosslinking of p-BA using $[\text{ChCl}][\text{ZnCl}_2]_2$ as solvent *via* TSE was incomplete. The isotherm of p-TPB-DES/TSE displayed a similar shape to that of p-BA-DES/TSE, with positive gas adsorbed values only appearing at $P/P_0 > 0.8$. The negative gas adsorbed values at low relative pressures resulted in a negative BET surface area, supporting the conclusion that hypercrosslinking of TPB using $[\text{ChCl}][\text{ZnCl}_2]_2$ as a solvent *via* TSE was unsuccessful.

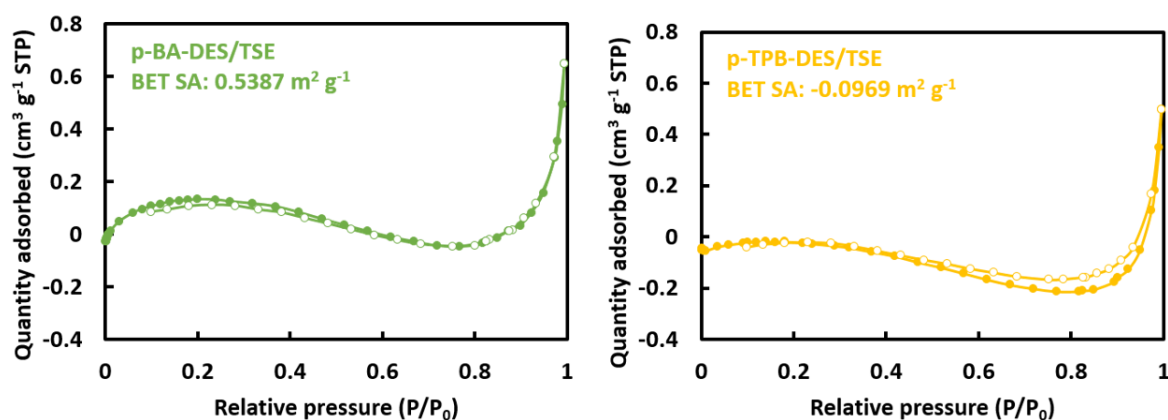


Figure 14 N_2 adsorption-desorption isotherm at 77 K of p-BA-DES/TSE (Left) and p-TPB-DES/TSE (Right). The adsorption and desorption points were represented as full and empty markers, respectively.

In term of productivity, despite the incomplete crosslinking of p-BA-DES/TSE, the current product yield allows for an estimation of the STY from TSE synthesis. Within an hour of operation, the synthesis process yielded approximately 63 % of p-BA-DES/TSE. Using Equation 1, the STY was calculated to be 117 mg mL⁻¹ day⁻¹. This STY value exceeded those from the batch synthesis of p-BA using DES and DCE by 4.7 and 2.4 folds, respectively. This suggests that synthesis *via* TSE can reduce reaction time, resulting in enhanced STYs compared to batch synthesis.

Equation 1 STY calculation for TSE process and the example calculation from the synthesis of p-BA-DES/TSE

$$\begin{aligned} STY_{TSE} &= \frac{\text{Throughput rate}}{\text{Barrel volume} \times \text{Extrusion passes}} \\ &= \frac{3g \text{ BA} \times 0.63 \text{ yield per hour} \times 1000 \text{ mg per g} \times 24 \text{ hour per day}}{48.3 \text{ mL} \times 8 \text{ passes}} \\ &= 117.4 \frac{\text{mg}}{\text{mL day}} \end{aligned}$$

The primary reason of the unsuccessful and incomplete crosslinking of these samples may be attributed to the evaporation of FDA. Since the boiling point of FDA is 42 °C and the operating temperature was set to 180 °C, it is possible that FDA evaporate and escaped through the exit of the extruder barrel. While the substitution of other external crosslinkers, *for e.g.*, trimethyl orthoformate, trimethyl orthoacetate, and triethyl orthoacetate has been proposed and has been successfully employed as crosslinker in HCP batch synthesis,³² these chemicals all have boiling points lower than 140 °C, which is still below the operating temperature for this synthesis. In the absence of an external crosslinker, the formation of crosslink bridges would depend on the functional group within the monomer itself, meaning it would utilise self-condensation or an internal crosslinking approach.¹⁶ Hence, the crosslinking of BA is possible due to the presence of –OH group, whereas the crosslinking of TPB is unachievable due to the absence of a functional group. As it was observed that p-BA from synthesis using DES *via* TSE was lightly crosslinked, as evidenced by the formation of brown solid particles distinct from the former liquid monomer and the positive value of BET surface area, further optimisation of the synthesis process should be investigated.

6.3.3. Conclusions, limitations, and suggestions

In conclusion, the current findings suggest that TSE holds promise as a synthetic apparatus for HCP synthesis using [ChCl][ZnCl₂]₂ as a solvent. TSE's autonomous mixing and heating align well with the solid handling requirements of the monomer and the ChCl and ZnCl₂ mixture. Notably, the issue of solid particle clogging, a common problem in continuous flow synthesis, was not observed in the synthesis *via* TSE. The significant advantage of employing TSE is the substantial improvement in STY compared to batch synthesis. However, achieving complete crosslinking of HCP with higher BET surface area requires further optimisation of operating parameters in the TSE process.

One of the limitations of HCP synthesis *via* TSE is that the synthetic approach only allows for self-condensation, as the addition of FDA was not effective in the open system of the extruder. Furthermore, monomers with halide groups should be avoided, as by-products like

hydrogen chloride could damage the extruder. Potential monomers for further investigation include 1,4-benzenedimethanol, as it resembles the structure of DCX,²⁹ and benzyl ether monomers, *for e.g.*, 4,4'-bis(methoxymethyl)biphenyl, 1,4-bis(methoxymethyl)benzene, and benzyl methyl ether, which contain ether functional groups similar to the structure of FDA.¹²⁸

Suggestions for optimising HCP synthesis *via* TSE revolve around the operating parameters. For instance, increasing the catalyst amount per mole of monomer, as indicated in batch synthesis research. Another parameter to consider is the order of feed input. In batch synthesis, ChCl and ZnCl₂ were mixed for 5 hours to achieve a homogenous solution. In the TSE synthesis experiment, however, the monomer was mixed together with solid ChCl and solid ZnCl₂ as they were fed simultaneously at the first section of the barrel. This non-homogenous DES may have affect the activity of DES,⁹⁹ resulting in a lower degree of crosslinking. Investigating the input order of the monomer into the second to sixth sections of the extruder barrel might allow the DES to homogenise before interacting with the monomers, potentially enhancing the activity of DES and yielding a higher specific surface area of HCP. Additionally, optimising the temperature control for each of the six sections could be explored as another parameter. The objective of these recommendation is to successfully attain a high specific surface area for the HCP product, reaching a minimum of 200 m² g⁻¹ to match batch-synthesised HCP using DES. Accomplishing this objective would position HCP synthesis using DES as a more benign alternative *via* TSE as an appealing choice for large-scale manufacturing manufacturers. In addition to providing HCPs with acceptable specific surface area HCPs, this approach offers the benefits of high STY, resulting in increased productivity and increase profitability, and the use of less hazardous chemical, which potentially improve long-term environmental impacts.

7. Overall conclusions and future outlook

This study has made significant strides in the intensification of HCP synthesis process, with an eye toward facilitating large scale manufacturing. The transition from traditional batch synthesis to continuous flow synthesis was successfully achieved, demonstrating the versatility of this approach through three distinct HCP species representing three major synthetic approaches. These species included internally crosslinked DCX, post-crosslinked polystyrene with a DCX crosslinker, and externally crosslinked polystyrene with a FDA crosslinker. To gauge the improvements brought about by continuous flow system in comparison to batch system, continuous flow synthesis was benchmarked against batch synthesis across four key aspects: 1) productivity, *i.e.*, the STY of the synthesis process, 2) textural property, *i.e.*, BET surface area of the HCP product, 3) performance ability, *i.e.*, CO₂/N₂ selectivity, and 4) environmental impacts related to certain applications - dye adsorption and CO₂ capture.

In terms of productivity, continuous flow synthesis increased STYs by 32, 117, and 68 fold for the internal, post-, and external crosslinking approaches, respectively, translating to STY values of 563, 718, and 842 mg mL⁻¹ day⁻¹. This remarkably enhancement underscores the competitiveness of continuous flow synthesis in aspect of productivity compared to the conventional batch process.

Regarding textural properties, the internally crosslinked, the post-crosslinked, and the external crosslinked HCPs synthesised *via* the continuous flow method exhibited BET surface areas of 950, 816, and 1092 m² g⁻¹, respectively. These values were lower than their respective batch-synthesised HCPs, with reductions of 1.5 %, 10 %, and 6 %, respectively. Additionally, the micropore volumes of internally crosslinked and externally crosslinked flow-synthesised HCPs increased by 570 % and 60 %, respectively, compared to their batch-synthesised counterparts. In contrast, post-crosslinked flow-synthesised HCP has a lower micropore volume, decreased by 4 %, compared to batch-synthesised HCP. These results confirm that HCP synthesised through the continuous flow system possess textural properties that are comparable to, or in some cases even superior to, those synthesised *via* the traditional batch process.

As a result of possessing slightly lower BET surface areas and higher micropore volumes in flow-synthesised HCP, the adsorption of CO₂ and N₂ at 1 atm and 298 K of internally crosslinked flow-synthesised HCP showed 3.5 % and 76 % reductions compared to batch-synthesised counterpart. The excellent CO₂ adsorption and the poor N₂ adsorption capacities led to a 850 % improvement in the selectivity of CO₂ over N₂ of internally crosslinked HCP synthesised through continuous flow, when compared to batch-synthesised counterpart. Conversely, the CO₂ and N₂ adsorption capacities for other HCPs synthesised *via* continuous flow were 24 % lower and 3 % higher for post-crosslinked HCP, and 32 % lower and 38 % lower for externally crosslinked HCP. These variations in adsorption capacities resulted in lower CO₂/N₂ selectivity values, with reductions of 24.5 % and 23 % for post-crosslinked and externally crosslinked HCPs, respectively, when compared to HCPs from batch synthesis. Overall, these outcomes suggest a range of performance capacities for flow-synthesised HCPs, from excellent to moderate, when compared to their batch-synthesised counterparts. This

indicates that HCP synthesised through continuous flow have practical potential for real-world applications.

In terms of environmental impacts, the continuous flow system for HCP synthesis demonstrated reduced environmental impacts across all endpoint indicators when synthesising the same quantity of HCPs compared to the batch method. This reduction can be attributed to lower electricity consumption, due to the 99 % shorter reaction time in continuous flow synthesis. When producing the required externally crosslinked HCPs for dye adsorption and CO₂ capture, the continuous flow synthesis exhibited higher Ecosystem quality endpoint impact score. It showed a 20 % increase for RB adsorption, a 27 % increase for UA adsorption, and a 36 % increase for atmospheric pressure CO₂ capture compared to batch synthesis. The required amount of post-crosslinked and internally crosslinked HCPs for CO₂ capture *via* continuous flow synthesis also resulted in 197 % and 36 % higher Ecosystem quality endpoint impact scores compared to batch synthesis. Additionally, there was a 19 % increase in the Human health endpoint impact score for continuous flow synthesis of internally crosslinked HCP. The higher environmental impact scores in continuous flow synthesis were primary attributed to lower product yields compared to the batch process. Future improvements to the reactor design (*for e.g.*, adjusting tube inner diameter and tube length), aimed at achieving higher product yields (even if not matching batch levels), could help mitigate these environmental impacts that tend to be higher in continuous flow synthesis. Nonetheless, it is crucial noting that beside these negative outcomes, all other endpoint impacts were lower when utilising the continuous flow system for dye adsorption and CO₂ capture, even though higher amount of HCPs were needed.

Furthermore, this study ventured into process intensification of HCP continuous synthesis using a more benign solvent, DES, as an alternative to conventional halogenated solvents like DCE. While the endeavour for this synthesis of HCP using DES as an alternative solvent remained within the field of continuous synthesis, it encountered challenges related to the infeasible design of continuous flow system. These challenges included difficulties in handling feeds, uneven heating, and inadequate mixing, which led to pre-crosslinking and low product yield. However, the introduction of the TSE system displayed potential to address these issues comprehensively. Based on the experimental findings, TSE has demonstrated promise in facilitating HCP synthesis using DES as a solvent. Nevertheless, further optimisation of the process is warranted to attain HCPs with acceptable specific surface area for practical applications. Future experiments should also encompass an environmental assessment of HCP synthesis *via* TSE using DES as a solvent, comparing it with batch synthesis using both DCE and DES as solvents. Thus, providing a comprehensive evaluation of this synthetic approach in terms of textural properties, productivity, and environmental impacts, as previously conducted with continuous flow synthesis of HCP in the conventional route.

In summary, this thesis introduced the implementation of a continuous flow system for HCP synthesis and highlighted its advantages over traditional batch synthesis, serving as a foundation for potential adoption of continuous flow method in industrial-scale production. The exploration of alternative synthesis method, continuous mechanosynthesis for HCP synthesis, coupled with the use of a more benign solvent, added a promising dimension to

further investigations that may establish it as a superior synthesis choice compared to continuous flow synthesis using conventional solvents. Moreover, environmental assessment and technoeconomic assessment are highly recommended for the large-scale HCP production using the aforementioned alternative synthesis method. Ultimately, this thesis has laid the groundwork for the intensification of the HCP synthesis process, aiming for improved productivity and enhanced environmental sustainability, with the hope of future implementation in larger-scale manufacturing operations.

8. References

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