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Abstract

Sustainable production methods for polymer membrane fabrication are gaining attention due to concerns about the toxicity of conventional fossil-derived solvents in the production process. In addition, the promotion of using chemicals from renewable source for synthesis processes among industries and researches has increased to decelerate resource depletion. As such, more benign and bio-renewable solvents, dihydrolevoglucosenone (Cyrene™) and 2-methyltetrahydrofuran (2-MeTHF), have been proposed as replacements for traditional fossil-derived solvents, n-hexane and dimethylformamide (DMF). In this work, a life cycle assessment (LCA) was employed to quantitatively evaluate the environmental impacts of using the aforementioned bio-renewable solvents versus fossil-derived solvents for fabricating 1 g of polymer membrane. The analysis adopted a cradle-to-gate perspective and assessed three endpoint impact categories: Human health, Ecosystems and Resources. Despite lower environmental impacts for producing bio-renewable solvents, using such solvents to fabricate membranes displayed a higher environmental impact score in all endpoint categories. This discrepancy was attributed to the lower yield of the membrane fabrication process when using bio-based solvents. This indicated that further work is needed to optimise membrane fabrication so that the benefits of using bio-based solvents can be maximised.

Keywords: Membrane fabrication, bio-renewable solvent, life cycle assessment, LCA

1. Introduction

Organic solvent nanofiltration (OSN) is a sustainable pressure-driven membrane separation process that enables organic solvent purification and valuable compound recovery. This membrane-based process offers lower energy consumption, milder operating conditions, and higher separation efficiency than traditional separation processes, such as, distillation and chromatography. [1] At the heart of OSN is the thin film composite polymer membranes, which are commonly fabricated *via* phase inversion and interfacial polymerisation. [2] Phase inversion is used to produce porous support layers while interfacial polymerisation is deployed for depositing a selective layer on the porous support. In industry, the non-solvent-induced phase separation (NIPS) approach is widely used for membrane production. [3] The NIPS process involves, first, producing a porous support *via* phase inversion of a polymer dope solution containing a synthetic polymer in an organic solvent. Following this, the porous support is soaked in an aqueous polyamine solution and subsequently immersed in a water immiscible organic solvent solution containing acyl chlorides, which react at the immiscible liquid interface to form the selective layer. [4] Typically, the organic solvents used in NIPS are derived from fossil fuels. Either dimethylformamide (DMF), dimethylacetamide (DMAc) or *N*-methyl-2-pyrrolidone (NMP) is used to prepare the polymer solution in the porous support production owing to their favourable physical properties, including their complete solubility in water and high boiling points. [5, 6] Ascribing to its ability to dissolve acyl chlorides whilst being water immiscible, n-hexane is used as the organic phase during formation of the selective layer.

The use of fossil-derived solvents during membrane fabrication may compromise the reported environmental sustainability of OSN. [7] These solvents contribute to environmental pollution throughout their lifecycle, from production to disposal. One well-known, long-term environmental issues is non-renewable resource exploitation, which is consequently associated with global sustainability and climate change issues. [8] Moreover, DMF, NMP and DMAc are categorised as 'substances of very high concern' per the UK REACH regulation because of their reproductive toxicity and n-hexane presents its own issues given its neurotoxic nature. [9, 10] Their use is subject to stringent regulations and it is intended that they are gradually phased out of use. As a result, traditional means of membrane fabrication is quickly becoming obsolete and the need for a less hazardous and safer alternative is becoming more urgent.

Bio-renewable solvents, derived from bio-based feedstocks, have gained attention as potential replacements for fossil-derived solvents in polymer membrane fabrication. [11-13] These bio-renewable solvents comply with the principles of green chemistry, which stipulate that hazardous solvents should be replaced with safer alternatives derived from renewable feedstocks. [14] The use of bio-based feedstocks as raw material tackles several of the issues associated with fossil fuel derived solvents, such as fossil fuel depletion, carbon dioxide emissions and supply security. [15] Incorporation of bio-renewable solvents has been reported in several organic synthesis processes, [16] including thin film composite polymer membrane fabrication. The use of bio-renewable solvents dihydrolevoglucosenone (Cyrene™) and 2-methyltetrahydrofuran (2-MeTHF) in the membrane fabrication study has been reported. [17] Cyrene™, derived from sawdust *via* the Furacell process, has physicochemical properties comparable to typically used

fossil-derived polar aprotic solvents during polymer solution preparation. [18] It does not have any of the same carcinogenic, mutagenic or reproductive toxicity issues as its fossil fuel derived counterpart. 2-MeTHF, a bio-based solvent derived from corncob, exhibits partial miscibility in water, making it a potential replacement for n-hexane during membrane fabrication. [19] This fabrication route represents a novel scenario where benign solvent alternatives are used throughout the membrane fabrication process, aiming to reduce the consumption of non-renewable resources, and consequently, improve the overall process sustainability.

The concept of sustainability, which encompasses environmental, economic, and social dimensions, has been vaguely claimed without quantitative measurement. To holistically and quantitatively approximate one key aspect of sustainability, specifically the environmental impact, in the context of membrane fabrication *via* the alternative bio-renewable solvents, a life cycle assessment (LCA) framework was employed. An LCA is a comprehensive environmental assessment technique developed to quantitatively evaluate the environmental load of a system. [20] The principle of LCA is to compile data on the material and energy flows exchanged with the environment over the life cycle of the product, starting from raw material acquisition, through the production process, product use, and final disposal or recycling, *i.e.* cradle-to-grave. This is then converted into potential contributions to several environmental impact categories.

LCAs have been commonly used to assess the sustainability of bio-based processes. [21-23] These studies are often carried out at various stages of process development to assess the environmental feasibility of a given production route. [24] Per the ISO 14040 [25] and

ISO 14044 [26] standards, an LCA can be split into four distinct stages. Goal and scope definition is the first step of an LCA, wherein the aim of the study is defined. Key information, such as the intended application of the study, functional unit (parameter to which all inlet and outlet flows are to be normalised) and system boundaries are determined. The second step is the life cycle inventory analysis (LCI), where input and output flow data are collected for each of the unit processes within the system boundary. The unit processes can be categorised into foreground and background systems. The foreground system encompasses the unit processes that are specific to the product system being evaluated, while the background system is comprised of the unit processes that are required to fulfil the foreground system, *e.g.* material inputs, waste treatment/disposal. The next step is the life cycle impact assessment (LCIA), in which the collected input and output data is used to calculate and assign results to several environmental impact categories. Finally, in the life cycle interpretation, conclusions are made from the findings and any limitations of the study are identified.

The purpose of this work was to investigate the environmental performance of a novel membrane fabrication route, [17] referred to as the green route, which used bio-renewable solvents (Cyrene™ and 2-MeTHF) compared to the conventional route wherein fossil fuel-based solvents (DMF and n-hexane) were employed. The aim of this green route was to replace the use of fossil-derived compounds, including solvents and polymers, in TFC membrane fabrication with bio-renewable, benign alternatives. An alternative material for fossil-derived polymers such as polyethersulfone, polyacrylonitrile and crosslinked polyimide, that are widely used in the fabrication of porous supports for TFC membranes is cellulose acetate. [27] A cradle-to-gate LCA was carried out for 1 g of each membrane, considering the production of all input materials, and employing the ReCiPe method to evaluate impact scores across three endpoint

categories: human health, ecosystems and resources. Despite the fact that the bio-based solvents were in general more environmentally friendly than their fossil-derived counterparts, it was found that across all endpoint impact categories, the green route exhibited worse environmental impacts. This was attributed to the poor yield of membrane fabrication when using bio-renewable solvents in traditional membrane fabrication methods. This clearly indicated that novel membrane fabrication methods should be developed to fully exploit the environmental benefits brought by bio-renewable solvents. Incorporating membrane use, especially in the OSN application, into the LCA was a suggestion for the future work, which may improve the environmental performance of the green route. This is particularly relevant, given recently proposed methods, such as spray coating, to enhance the separation performances of bio-renewable-derived membranes. [28]

2. Experimental method

2.1. Membrane fabrication

2.1.1 Bio-renewable solvent employment (green route)

The procedure for membrane fabrication comprised of two-steps: (1) preparation of a porous support layer using one-step deacetylation-coagulation, (2) production of the polyamide film using interfacial polymerisation (Figure 1).

Cellulose acetate is typically dissolved in co-solvent systems comprising DMF or NMP and acetone. [29, 30] In this work, we chose to use Cyrene™ to replace NMP or DMF for membrane fabrication as this is a proven strategy that improves the sustainability of membrane fabrication. [31-33] However, this is the first time Cyrene™ is used to fabricate cellulose acetate membranes. As such, we compared the Hansen solubility parameters of

cellulose acetate, Cyrene™ and NMP and DMF revealed that the relative energy distance (RED) values for cellulose acetate with Cyrene™, NMP and DMF were 1.05, 0.87 and 0.36, respectively. [34] This indicated that Cyrene™ may not dissolve cellulose acetate as well as NMP. To improve the solubility of cellulose acetate in Cyrene™, we added acetic acid into Cyrene™, reducing the RED value from 1.05 to 0.89. Hence a 3:1 ratio of Cyrene™ and acetic acid was chosen here. This co-solvent system only fully dissolved cellulose acetate at 80 °C after 8 hours of continuous stirring. Based on these observations, we prepared a 50 mL polymer dope solution was prepared by dissolving 17.5 w/v % cellulose acetate in mixture of Cyrene™ and acetic acid (3:1) at 80 °C for 8 hours using a heated stirrer. This solution was rest overnight to allow any bubbles to dissipate. The dope solution was cast onto a glass plate using a casting knife (Elcometer 3700) and immersed in the coagulation bath containing 0.05 M KOH and DI water (10 L). After removing supports from the bath, they were rinsed with 30 mL of DI. The porous support was then taped to a glass plate and soaked in 30 mL aqueous solution of 3 w/v% piperazine for 2 minutes. The amine-loaded support was then pressed with a roller and wiped to remove any excess solution. Subsequently, it was immersed in 30 mL solution of 3 w/v % trimesoyl chloride in 2-MeTHF for 4 minutes and then rinsed with 30 mL of DI water.

2.1.2. Fossil fuel-based solvent employment (conventional route)

A similar protocol is followed with a few variations for the conventional route. The polymer dope solution comprised of 17.5 w/v % cellulose acetate in DMF, the porous support was soaked in a 2 w/v % piperazine solution for 2 minutes and the amine-loaded support was soaked in 0.1 w/v % trimesoyl chloride in n-hexane for 2 minutes. It is

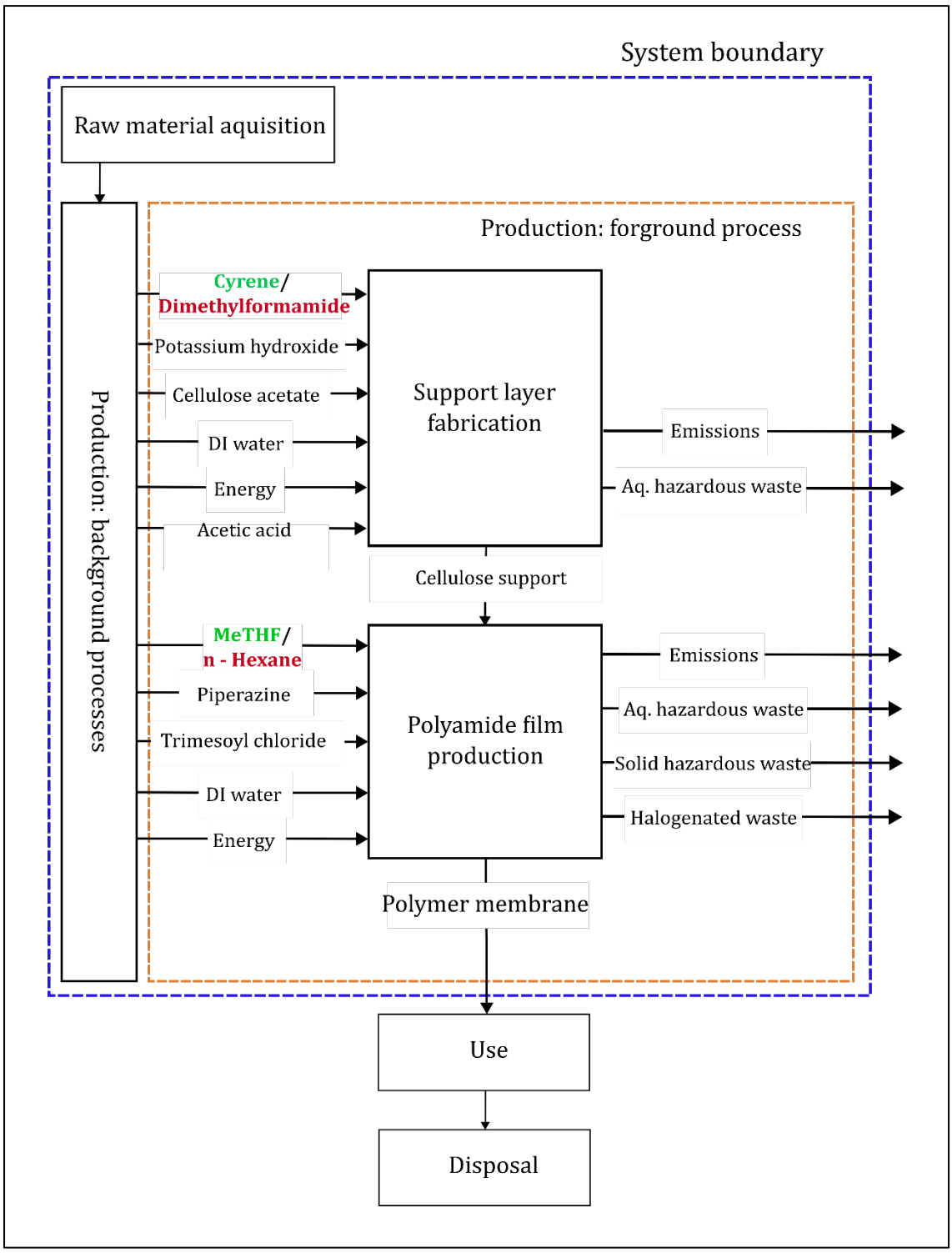
important to note that the conventional route did not necessitate the use of acetic acid and involved lower concentrations of both piperazine and trimesoyl chloride.

2.2. Goal and scope definition

A comparative LCA was carried out per the ISO 14040 and ISO 14044 standards, to assess the environmental impacts of bio-renewable (green route) and fossil fuel-based (conventional route) solvent employment in membrane fabrication. A functional unit of 1 g of membrane was selected for both production routes.

This study took a cradle-to-gate perspective. The boundary covered the production of the membrane including the raw material extraction process. The use of the membranes in any application and end-of-life disposal were not considered as shown in Figure 1. A cradle-to-gate assessment is similar, in terms of scope, to other studies, which consider bio-based production routes at the laboratory scale. [21, 35]

Due to limited data availability, waste and emission flows, and transportation of materials were omitted from the system boundary. The foreground process was modelled based on UK-specific data, given that the membranes were produced within a laboratory at the University of Edinburgh, Scotland. Average European data was used to model the background processes.



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194 *Figure 1 Block flow diagram of membrane fabrication for both green and conventional*
195 *membrane fabrication. System boundary and foreground system are highlighted by blue*
196 *and orange dotted lines respectively*

2.3. Life cycle inventory analysis

LCI data was collected in accordance with the system boundaries that were specified in the goal and scope definition phase of the LCA. The laboratory scale membrane fabrication process was defined as the foreground process. Primary data for chemical and electricity inputs were provided by Akram. [17] Data for the background system was collected from secondary sources such as published LCA studies, LCI databases, or calculated.

2.4. Life cycle impact assessment

The LCIA was carried out using SimaPro (Version 8.0), a widely-used LCA software. This software facilitates key steps of the LCIA, including classification (assigning flows to relevant environmental impact categories), characterisation (determining magnitude of each flow on a given impact category), and normalisation (comparing the values to a reference value).

Within SimaPro, the LCIA method used was ReCiPe (Version 1.10). This method is a "black-box" LCIA framework that allows the calculation of 18 midpoint indicators and 3 endpoint indicators, the widest set of impact categories by any LCIA method and the most commonly used method in the chemical industry. [36, 37] The 18 midpoint impact categories are as follows: climate change, ozone depletion, terrestrial acidification, freshwater eutrophication, marine eutrophication, human toxicity, photochemical oxidant formation, particulate matter formation, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionising radiation, agricultural land occupation, urban land occupation, natural land transformation, water depletion, metal depletion, and fossil

depletion. These are grouped to determine 3 endpoint categories: human health, ecosystems and resources. The relationship between these midpoint and endpoint impact categories was presented in the supplementary Information. The reader can refer to the literature from Goedkoop *et al.* [38] for a comprehensive list of the ReCiPe characterisation factors (>70,000), midpoint impact categories, indicators, normalisation references and endpoint indicator normalisation references used in this study.

3. Results and discussion

3.1. Life cycle inventory

3.1.1 Foreground process

A summary of the LCI results for membrane fabrication *via* both production routes was presented in Table 1.

Table 1 Life cycle inventory for the production of 1 g of polymer membrane.

	Conventional route	Green route
Material inputs		
Cellulose acetate (g)	8.21×10^{1}	3.62×10^{2}
Cyrene™ (g)	-	1.28×10^{3}
DMF (g)	3.87×10^{2}	-
Acetic acid (kg)	-	4.26×10^{2}
Potassium hydroxide (g)	4.74×10^{2}	2.09×10^{3}
Water, deionised (L)	1.69×10^{2}	7.46×10^{2}
Piperazine (g)	5.63×10^{0}	3.72×10^{1}
Trimesoyl chloride (kg)	2.81×10^{-1}	3.72×10^{1}
2-MeTHF (mL)	-	1.240×10^{3}
n-Hexane (mL)	2.81×10^{2}	-
Utilities		
Electricity (kWh)	2.10×10^{0}	9.26×10^{0}
Other information		
Mass of support produced (g)	6.72×10^{0}	2.96×10^{1}
Yield ($g_{membrane}/g_{support}$)	1.49×10^{-1}	3.40×10^{-2}

3.1.2 Background system

The background processes data were primarily collected from the ecoinvent v3.0 database. [39] This is a widely used LCI database, containing flow input and output data on over 12,000 processes and products. The absent data of some processes from ecoinvent library was determined from a combination of industrial sources, literature and stoichiometric calculations. A summary of the data collection methods was provided in Table 2 and a detailed account of all new LCI datasets were presented in the Supplementary Information.

Where relevant, biogenic carbon neutrality was assumed. By definition, biogenic carbon is the carbon accumulated in biomass or other renewable feedstocks during growth. For any unit process wherein materials derived from renewable feedstocks were incinerated, the carbon dioxide emissions were neglected. [40] Furthermore, sequestration of any emitted carbon dioxide following incineration was taken as an overall credit to the process. Such an analysis is commonly used in LCA studies. [41] Allocation procedures for the modelled processes varied on a case-by-case basis, and an account of this can be found in the relevant Supplementary Material. Of note is the allocation procedure associated with biomass cultivation. Often the biomass used in the production of green solvents are waste products from other processes, *e.g.* corncob used for 2-MeTHF production and sawdust for Cyrene™ production. In this study, it is assumed that in the relevant processes, biomass is a waste co-product stream in its production process. Hence, any environmental load associated with its cultivation can be omitted from the study.

257 *Table 2 Summary of life cycle inventory data collection methods for backgroud unit*
258 *processes*

Material	Production route	Specificities	Source
Green membrane production	Non-solvent induced phase separation	Very high	First-hand collection
Conventional membrane production	Non-solvent induced phase separation	Very high	First-hand collection
Cellulose acetate	Acetylation of cellulose	Medium	Calculated from patent literature [42, 43]
Cyrene™	Hydrogenation of levoglucosenone	Medium	LCI data from industry
DMF	Reaction of dimethylamine with carbon monoxide	Medium	ecoinvent v3.0
Acetic acid	Carbonylation of methanol	Medium	ecoinvent v3.0
Potassium hydroxide	Electrolysis of potassium chloride	Medium	ecoinvent v3.0
n-Hexane	Molecular sieve separation of naphta	Medium	ecoinvent v3.0
2-MeTHF	Hydrogenation of 2-methylfuran	Medium	LCI in literature [44]
Piperazine	Reaction of 1,2-dichloroethane with ammonia	Medium	Stoichiometric calculation
Trimesoyl chloride	Reaction of trimesic acid with thionyl chloride	Medium	ecoinvent v3.0
DI water	Ion exchange	Medium	ecoinvent v3.0
Electricity	Electricity mix	Medium	ecoinvent v3.0

259 * LCI data calculation framework used in this study was developed and implemented by ecoinvent
260 (the primary database used for this LCA). [45-47]

261 **3.2. Environmental impact comparison of solvent production**

262 Figure 2 presents the normalised environmental impact score for each of the end-point
263 impact categories for both Cyrene™ and DMF production. A higher impact score indicates
264 that the route created more environmental impact compared to another route and is
265 thereby worse. A score below zero indicates that the process receives a credit or benefit
266 that offsets the environmental load from all previous stages. It can be seen that the
267 production of 1 kg of Cyrene™ has a lower environmental load compared to the

production of 1 kg of DMF across all three impact categories. This difference is influenced by two key factors. Firstly, the production of Cyrene™ involves the incineration of waste char to generate the required heat and electricity. The study, as detailed in the background system datasheet (Supplementary Information), treats biogenic carbon emissions from this process as neutral. In contrast, DMF production faces environmental consequences due to emissions associated with process energy generation. This is particularly important given the energy-intensive nature of DMF purification during production – attributed to its high boiling point and solubility characteristics**.** Secondly, the production of Cyrene™ receives an additional credit earned from excess energy exports. This results in a consistently lower (and below zero) environmental load of Cyrene™ production.

It is worth noting that Cyrene™ production *via* the Furacell process (as modelled in this study) is currently the only industrial-scale production process. However, this process remains at the pilot-scale. There are plans to develop a scaled-up plant, increasing the production capacity from 50 tonnes to 1000 tonnes. The LCA practitioner has been informed that the data provided for Cyrene™ production does not reflect the scaled-up plant and that further reductions in environmental load are anticipated. It is challenging to incorporate this information into the LCA at this time as the plant is not operational yet. Future iterations of the LCA should incorporate the most up-to-date process data available to accurately assess the environmental impact of the scaled-up production.

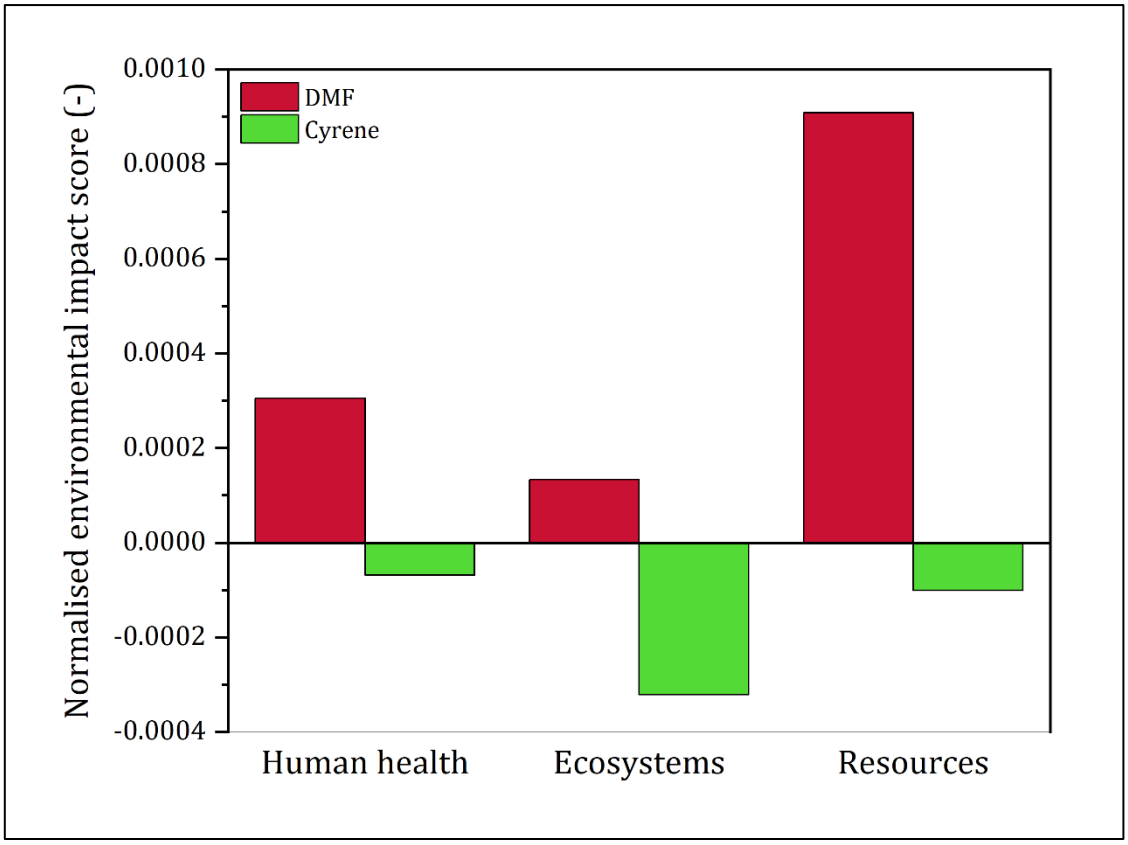

Figure 2 Normalised environmental endpoint impacts for Cyrene™ and DMF production (1 kg)

Figure 3 presents the normalised environmental impact score for each of the end-point impact categories for 2-MeTHF and n-Hexane production. 2-MeTHF presents a lower environmental impact score for two of three environmental impact categories, namely ecosystems and resources. However, the impact to the human health is higher than that of n-hexane. Raw material manufacturing, specifically 2-methylfuran, stands out as the primary contributor to this impact category. The root cause of this impact lies in poor yields in further upstream background processes. Similar to Cyrene™ production, 2-MeTHF production utilises biogenic waste solvent and accrues additional credits for excess energy exports. These credits, although favourable, are insufficient to fully offset the environmental impact of 2-MeTHF production.

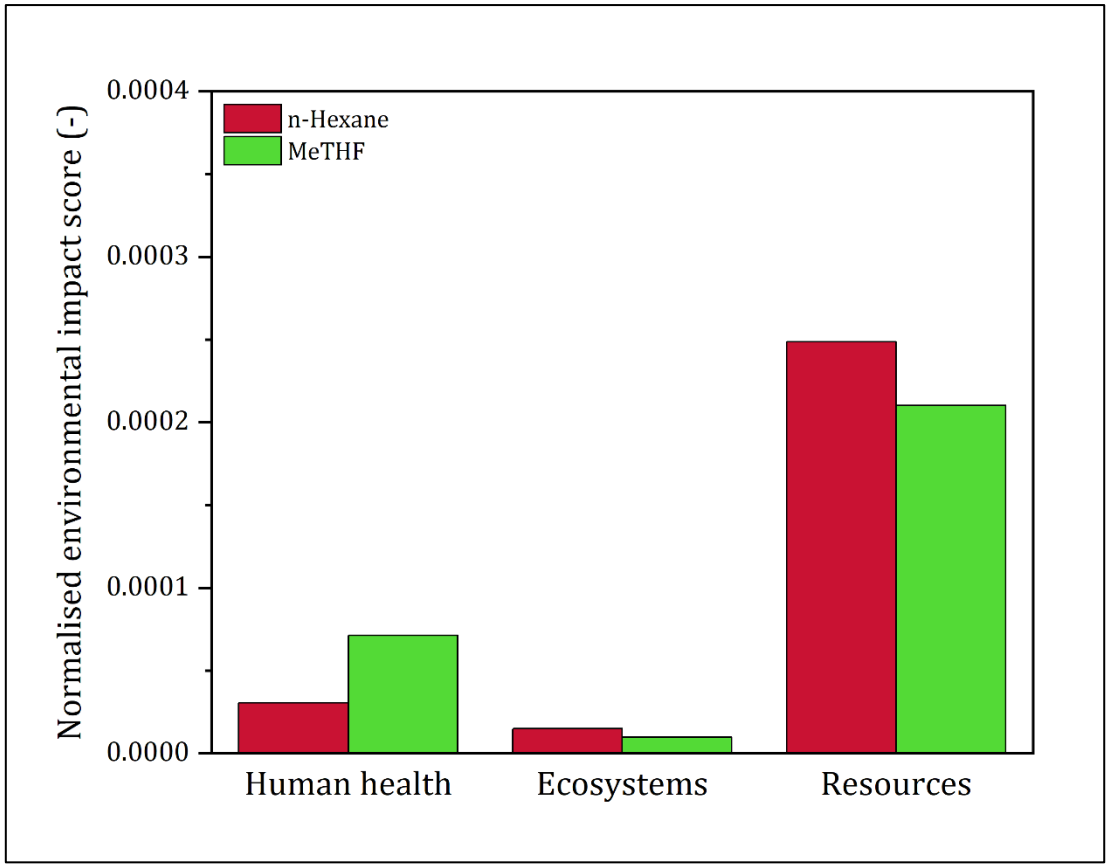

Figure 3 Normalised environmental endpoint impacts for 2-MeTHF and n-Hexane production (1 kg)

3.3. Environmental impact comparison of membrane fabrication via green and conventional methods

Figure 4 presented three environmental end-point impacts of the membrane fabrication process *via* conventional and novel green routes. From the figure, membranes produced from green route showed significantly higher environmental impact scores across all categories. The green synthesis impact scores were 256 %, 135 % and 227 % higher for human health, ecosystems and resources, respectively. These higher impacts can be attributed to the approximately 4.4 times lower yield of the green production route (Table 1). However, Akram reported that 10-fold more trimesoyl chloride was required to fabricate a dense polyamide selective layer when 2-MeTHF was used instead of n-hexane as the organic phase during interfacial polymerisation. This was most likely

attributed to the better water solubility of 2-MeTHF than n-hexane, where organic solvents with water solubility tend to require more monomer reactants to form dense polymer films. [48] Optimisation of the yield is necessary to reduce the overall environmental impact of this fabrication route. Considering the challenges associated with the replacement of both solvents (i.e., incomplete polymerization and bubble formation), exploring Cyrene™/hexane and DMF/2-MeTHF systems, where only one solvent is replaced, presents a promising path for further research.

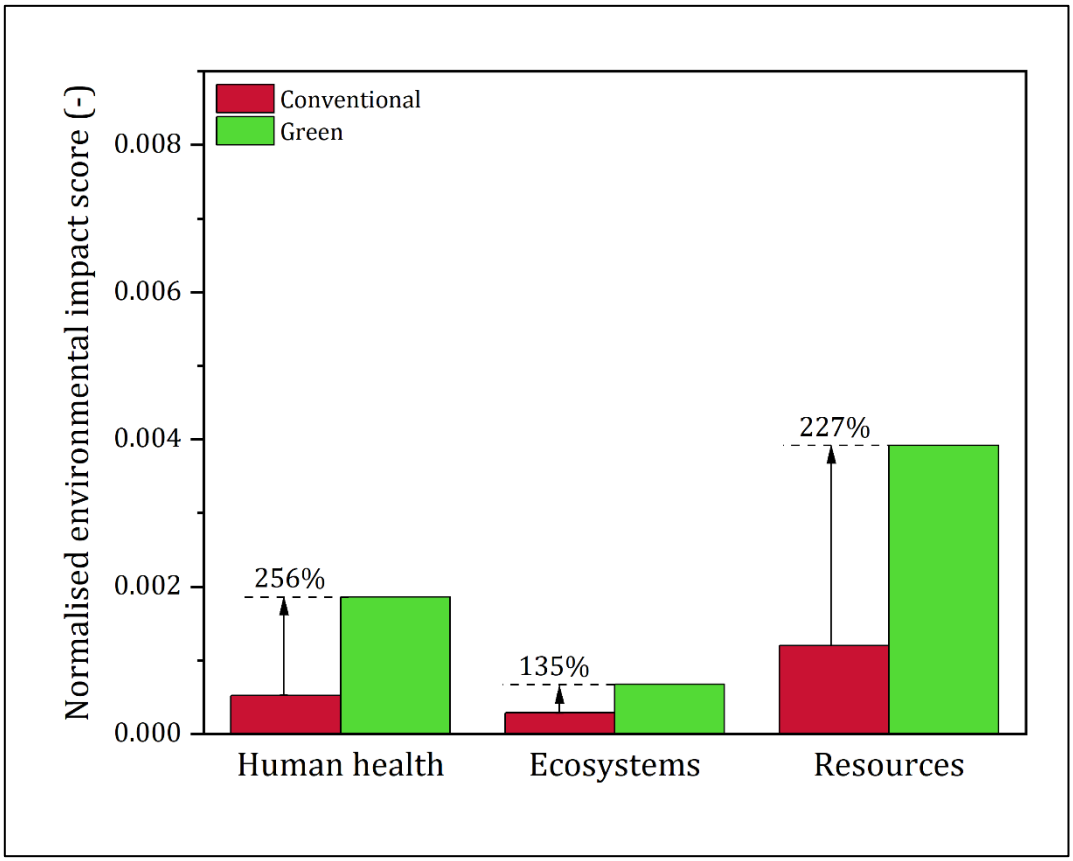

Figure 4 Normalised environmental endpoint impacts for membrane fabrication (1 g) using bio-renewable and fossil fuel-based solvents. The percentage increase is noted.

4. Conclusions and Suggestions

The environmental impact assessment of the thin film composite polymer membrane fabrication process employing novel green solvents (Cyrene™ and 2-MeTHF) was conducted. The traditional membrane fabrication using fossil fuel-derived solvents (DMF and n-hexane) was used as a benchmark for the comparative assessment. Through the standard LCA framework, the overall environmental impact of the fabrication process of the membranes produced from bio-renewable solvents was higher. This was due to lower membrane yield from the green route. This outcome indicated that the substitution of the bio-renewable solvent in a process could not ensure that the process would automatically become more sustainable, and further process development is crucial.

However, this work only considered a partial stage of the membrane's life-cycle, the possibility that the environmental impact contribution from the membrane produced from Cyrene™ and 2-MeTHF would trade-off in later stages of life. According to Akram's research, the membranes from the green route displayed higher permeance and rejection rates than the membrane from the traditional route. An increased permeance corresponded to lower energy consumption and, consequently, reduced environmental impact. Hence, consideration of membrane use could potentially serve as a benefit to the green production route.

Several suggestions should be taken into consideration for the future work in order to improve the feasibility and reliability of the assessment. Monte Carlo simulation should be carried out to account for uncertainties and variability in the input parameters and model assumptions. It is also recommended that an LCA should be carried out for a scaled-up version of the process presented here. This would involve implementing a pilot-scale production. By doing so, it would become possible to identify any differences

between the two processes, such as the use of different equipment, chemicals, and reagents. Additionally, heat integration and solvent recycling should be taken into account to maximise the sustainability of the process.

Beside the improvement for the future environmental assessment, the suggestions for experimental section has also been provided as following. Other than improving membrane fabrication yield, there is also a need to explore the use of alternative membrane fabrication technologies to improve the green metrics of using bio-renewable solvents for membrane fabrication. For e.g., the use of green solvents in membrane fabrication typically results in lower separation performances. We have recently overcome this trade-off between sustainability and membrane separation performances by using spray-coating to fabricate thin film composite membranes. [28] Another strategy that can potentially address the challenges of improving green metrics of membrane fabrication is to identify alternative materials for both the selective and porous support layers. [7]

CRediT authorship contribution statement

Aiman Arif: Software, Formal analysis, Writing – Original Draft, Writing – Review & Editing, Visualisation; **Nadhita Chanchaona:** Conceptualisation, Methodology, Writing – Review & Editing; **Cher Hon Lau:** Conceptualisation, Writing – Review & Editing, Supervision.

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