

Comparison Between Conventional Solvothermal and Aqueous Solution-based Production of UiO-66-NH₂: Life Cycle Assessment, Techno-economic Assessment, and Implications for CO₂ Capture and Storage

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Abstract: Metal-organic frameworks (MOFs) are a new class of materials that has shown great potential in catalysis, sensing, separations, and carbon capture and storage. Conventionally, MOFs are synthesized at lab-scale using organic solvent-based systems, leading to high environmental burdens and high operating costs, which ultimately hinders the large-scale production and application of MOFs. Aqueous synthesis of MOFs overcomes such difficulty by eliminating the organic solvent, which makes it an environmental-friendlier and economically-favorable alternative to the current production method. However, further

quantitative analysis is required to compare the environmental and economic performances of the two methods. Here, we used life cycle assessment (LCA) coupled with techno-economic analysis (TEA) to evaluate the environmental and economic performances of different UiO-66-NH₂ production methods. When the solvothermal method was replaced by the aqueous solution-based method, the LCA and TEA results suggest the environmental burdens and cost of UiO-66-NH₂ production were reduced by up to 91% and 84%, respectively. By using aqueous solution-based method, the cradle to gate carbon footprint and production cost of UiO-66-NH₂ were estimated to be 43 kg CO₂ eq/kg and \$15.8/kg, respectively. We further applied our LCA results to reassess the role of UiO-66-NH₂ in carbon capture and storage (CCS) and compare its environmental performance with current benchmark (amine-based solvent). Our results show that UiO-66-NH₂ could potentially have better environmental performance than the amine-based solvent if the number of regeneration cycles is greater than 1513. This work is the first comprehensive LCA-TEA study that quantifies the substantial environmental and economic benefits of using the aqueous solution-based systems to produce UiO-66-NH₂, and the analysis in this work is intended to be a starting point for further systematic studies on the full life-cycle impacts of MOFs.

1. Introduction:

Metal-organic frameworks (MOFs) are a new class of materials, consisting of metal ions or clusters coordinated with organic linkers [1-3]. MOFs are known for their high porosity, uniform and tunable pore size, good crystallinity, and a high degree of chemical tunability [1-3]. As such, MOFs have been applied either independently in catalysis [4-6], sensing [7-10], and gas storage [11-16] or in hybrid materials in gas separation [17-20], ion sieving [21-23], and desalination [24-27], and MOFs are expected to play a more important role in high-impact applications in the near future [8, 28, 29].

Despite their huge potential in various applications, most MOFs are currently synthesized at lab-scale, and several challenges must be resolved before MOFs are produced at/above pilot-scale (e.g., the annual production rate is at least on the order of 10s of kilograms) [30-32]. These challenges mainly arise

from two aspects, the process economic feasibility and the process environmental impacts [30-33]. The process economic feasibility has two significant measures [34, 35], the production cost (e.g., capital cost and operating cost) and the process space-time yield (STY) [33, 36, 37]. The first measure, production cost, is an indicator for the product market price that makes the process breakeven. The lower the production cost, the higher the product economic favorability is at the same market price. The second measure, process STY, is an indicator for the effectiveness of the space and time usage of the process [33, 36, 37]. The process STY contributes to the product economic favorability in two manners. As the process STY increases, the same production line produces more products in its lifetime, so the effective capital cost decreases while the total product sales increases. Hence, a process with lower cost and higher STY is desired for the MOFs production [33, 36, 37]. The process environmental impacts, on the other hand, measures the environmental burdens (e.g., greenhouse gas emissions and water pollution) the synthesis generates and is an indicator for the process sustainability [38-40]. The process environmental impacts, although often overlooked, are as important as the process economic feasibility. They could be even more significant if the produced MOFs are used for sustainability-related applications [13, 41-46] (e.g., greenhouse gas capture/storage and energy storage). In other words, if MOFs were to be used for those applications, the environmental benefits they create (e.g., the amount of greenhouse gas captured/transferred) in their lifetime must surpass the environmental burdens their production process creates, otherwise the rationality of those applications might be jeopardized. To date, the lab-scale synthesis of many MOFs (e.g., ZIF-8, HKUST-1 and UiO-66 derivatives) is not attractive enough from either the process economic feasibility aspect or the process environmental impacts aspect, and these limitations are likely caused by the synthesis method of those MOFs [30-33].

Conventionally, the lab-scale synthesis of many MOFs is done via the slow nucleation-growth in organic solvents (e.g., solvothermal synthesis of UiO-66 derivatives would take 12 to 24 hrs) [30-33, 47], and such synthesis methods have two major drawbacks. First, the slow nucleation-growth process leads to long batch-to-batch time which lowers STY [30-33]. Second, the use of a large amount of organic solvents

greatly increases the production costs and creates significant environmental burdens [30-33]. As such, finding better alternatives (i.e., environmentally friendly and/or cost-effective alternatives) for the conventional slow organic solution-based synthesis of MOFs becomes an urgent need, and more recent efforts have been made to develop rapid aqueous-solution based synthesis methods of MOFs [33, 48-52]. In our recent work, Huelsenbeck *et al.* reported a generalized aqueous solution-based approach for the rapid synthesis of several MOFs (e.g., synthesis of UiO-66(-NH₂), ZIF-L and HKUST-1 within 10 min) and systematically studied the effects of solution chemistry on both the process STY and the product quality (e.g., surface area and defects) [33]. For all MOFs studied, the aqueous solution-based process has higher STY than the conventional organic solution-based process, and the quality of some MOFs (e.g., UiO-66-NH₂ and HKUST-1) obtained from the aqueous solution-based is comparable to their counterpart obtained from the organic solution-based process [33]. These findings encourage us to further investigate the environmental and economic benefits of using the aqueous solution-based process as an alternative for the organic solution-based process in the MOFs production, and we will quantify those benefits via life-cycle analysis (LCA) and techno-economic assessment (TEA). Both LCA and TEA are useful tools in the analysis of novel-material productions, and their applications have also been extended to the MOFs production in the recent years by few pioneer studies [46, 53]. For example, Grande *et al.* carried out LCA on CPO-27-Ni production via different synthesis approaches [53], and DeSantis *et al.* conducted TEA on MOF adsorbents, including Ni₂(dobdc), Mg₂(dobdc), Zn₄O(bdc)₃, and HKUST-1[46]. However, these studies only considered one aspect of the MOF productions, and none of them further applied the LCA/TEA results to justify the applications of the studied MOFs. Hence, comprehensive LCA-TEA studies on the MOF productions are necessary to fill the knowledge gap, and ideally, such studies should relate the productions to the applications of the target MOFs.

In this work, UiO-66-NH₂ was selected as the target MOF due to its successful synthesis from the aqueous solution-based system and its great potential in applications like gas separation, carbon dioxide capture and ion sieving etc [21, 43, 44, 54-56]. The overall goal of this work is to evaluate and compare the

environmental and economic performances of the conventional solvothermal production and the aqueous solution-based production of UiO-66-NH₂ and apply the analysis results to provide insights on the use of UiO-66-NH₂ in carbon capture and storage (CCS). This goal is further divided into four specific objectives. First, the lab-scale synthesis of UiO-66-NH₂ using the conventional solvothermal system and the aqueous solution-based system was analyzed, and both systems were scaled up to their corresponding hypothetical pilot-scale productions using chemical engineering design criteria [57, 58]. Next, LCA was applied to both hypothetical pilot-scale productions to evaluate their overall environmental impacts and analyze the contribution of each component to the overall impacts. Further, TEA was applied to both production methods to assess their economic feasibility and investigate the distribution of the costs. Finally, the LCA results were used to justify the use of UiO-66-NH₂ in CCS, and suggestions were made on the potential directions that would make UiO-66-NH₂ a better candidate in CCS. To the best of our knowledge, this work is the first comprehensive LCA-TEA study on UiO-66-NH₂ productions via solvothermal and aqueous-based systems, and we believe the results of this work will motivate further studies on the sustainable and economical productions and feasible applications of UiO-66-NH₂ as well as a vast majority of other MOFs.

2. Method

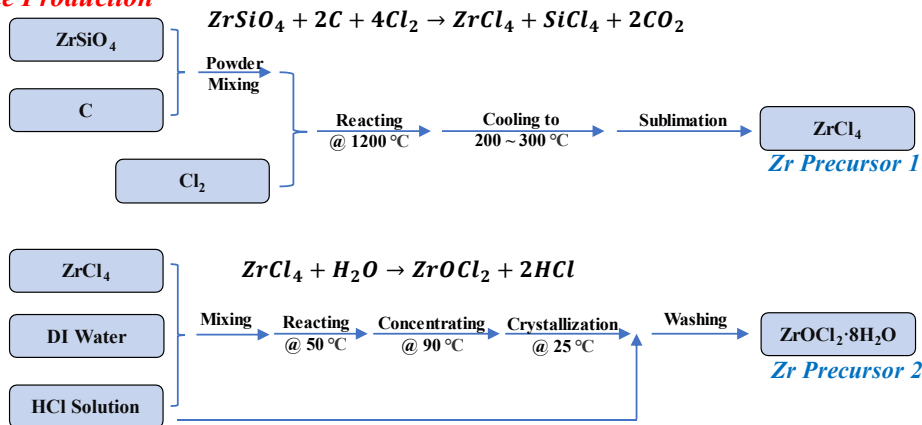
The accuracy and comprehensiveness for any LCA-TEA study depend on the description of the process, the choice of the system boundary, the data availability and the calculation methods [38-40]. Therefore, the process associated with UiO-66-NH₂ was described first in section 2.1, followed by the system boundary selection in section 2.2. The calculation methods for LCA and TEA were presented in section 2.2 and 2.3, respectively.

2.1 Process description

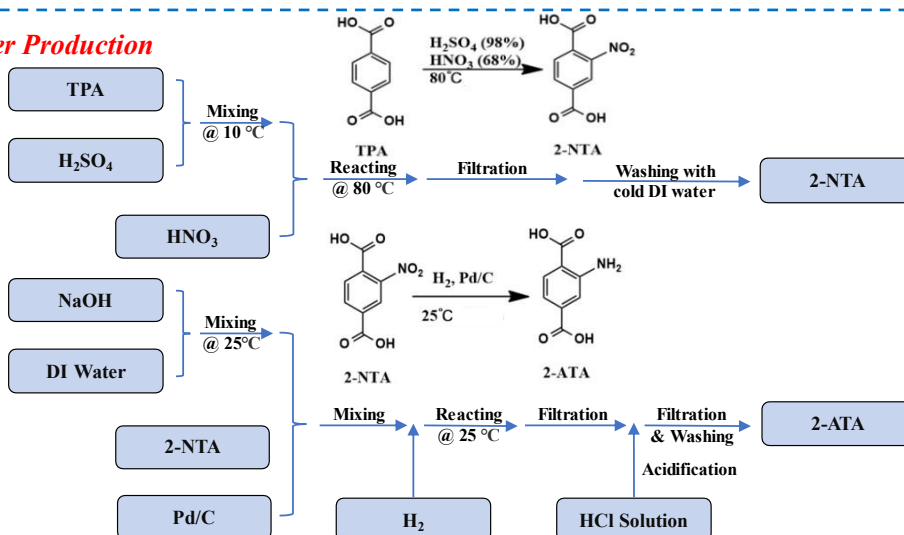
The ultimate goal of this study is to examine the environmental and economic performances for the pilot-scale production of UiO-66-NH₂ using the conventional solvothermal system and the aqueous solution-based system. However, the life cycle impact data for three key components, zirconium

tetrachloride ($ZrCl_4$), zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and the 2-aminoterephthalic acid (2-ATA), were not available in the Econivent v3.6 database [59]. Therefore, we decided to include the production of these three components in the process description to calculate their life cycle impact data and estimate the price of 2-ATA. A brief block flow diagram for all associated processes is presented in Figure 1.

Zr Source Production



Linker Production



UiO-66-NH₂ Production

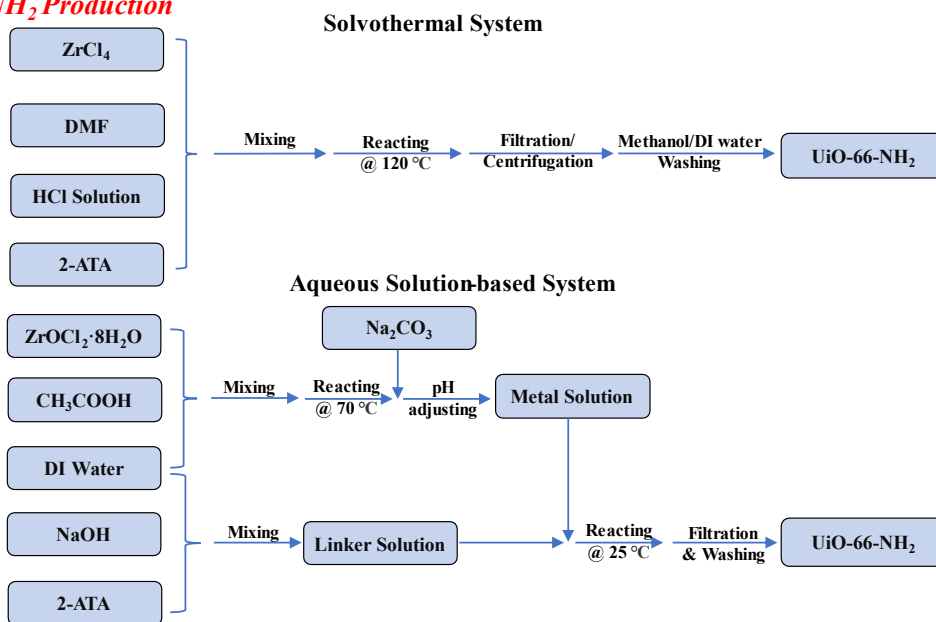


Figure 1. Brief block flow diagram of the Zr source production (top box), the 2-ATA linker production (middle box), and the UiO-66-NH₂ production (bottom box). These processes are either well-established in industry or representative at lab-scale [33, 60-66]. In brief, ZrCl₄ is fabricated from zircon via chlorination, ZrOCl₂·8H₂O is obtained from ZrCl₄ via hydrolysis, 2-ATA is synthesized from TPA via nitration and hydrogenation, and UiO-66-NH₂ is produced using either the combination of ZrCl₄ and ATA in DMF (solvothermal system) or the combination of ZrOCl₂·8H₂O and 2-NTA-Na₂ in water (aqueous solution-based system) [33, 60-66]. In the hypothetical pilot-scale production of UiO-66-NH₂, only 2-ATA and UiO-66-NH₂ are produced on site (i.e., Zr sources are purchased). Hence, the information from all three boxes was used in LCA, while the information from the middle and the bottom box was used in TEA.

2.1.1 Production of ZrCl₄, ZrOCl₂·8H₂O and 2-ATA

As shown in Figure 1, two types of Zr source, ZrCl₄, and ZrOCl₂·8H₂O, were used in UiO-66-NH₂ productions. The ZrCl₄ is synthesized from the high-temperature chlorination reaction of zircon (ZrSiO₄), using charcoal as the reducing agent and chlorine gas as the chlorine source [61]. The post-reaction gaseous mixture is cooled down to allow for the sublimation of ZrCl₄, and the obtained ZrCl₄ can be directly used in other productions without further purifications. The ZrOCl₂·8H₂O is obtained from the direct hydrolysis of ZrCl₄ in a dilute hydrochloric acid (HCl) solution. The post-reaction mixture is first concentrated at elevated temperature and then cooled down to room temperature for crystallization [62-64]. The crude ZrOCl₂·8H₂O is washed with an HCl solution, and the purified ZrOCl₂·8H₂O is used in other productions. A more detailed process description that includes the mass of the chemicals and the reaction conditions could be found in the Supporting Information (Page 2-3).

The linker, 2-ATA, is synthesized from a two-step nitration-hydrogenation reaction of terephthalic acid (TPA) [65, 66]. In the first step, a nitro group is introduced to the TPA by the nitration reaction at elevated temperature, using concentrated nitric acid (HNO₃) as the nitration reagent and concentrated sulfuric acid (H₂SO₄) as the dehydrator [64]. The post-reaction mixture from this step is first cooled down

to room temperature and then filtered to obtain the crude product, 2-nitroterephthalic acid (2-NTA). The crude 2-NTA is further washed with DI water prior to the hydrogenation reaction [66]. In the second step, the nitro group is reduced to the amino group by the aqueous solution hydrogenation reaction of disodium 2-NTA (2-NTA-Na₂) at room temperature, using palladium-on-carbon (Pd/C) as the catalyst and hydrogen gas as the hydrogen source. The post-reaction mixture from this step is first filtered to recover Pd/C and then acidified to precipitate 2-ATA. The 2-ATA is obtained by filtration, and is further washed with DI water prior to the UiO-66-NH₂ production. A more detailed process description that includes the mass of the chemicals and the reaction conditions is available in the Supporting Information (Page 3-4).

2.1.2 Production of UiO-66-NH₂

The production of UiO-66-NH₂ is achieved from both the conventional solvothermal system and the aqueous solution-based system [33, 60]. In the conventional solvothermal system, ZrCl₄ and 2-ATA are co-dissolved in DMF, and this DMF mixture is acidified with an HCl solution [60]. The acidified DMF mixture is heated at elevated temperature to allow for the formation of UiO-66-NH₂ *via* slow nucleation and growth. The post-reaction mixture is first cooled down to room temperature, and the UiO-66-NH₂ is then separated from the mixture by filtration or centrifugation. The obtained crude UiO-66-NH₂ is washed with methanol or water to remove any residual DMF and unreacted linker/metal components. In the aqueous solution-based system, the zirconium-oxo-cluster solution (referred to as the metal solution for brevity) and the linker solution are prepared separately [33]. The metal solution is prepared by heating the ZrOCl₂·8H₂O in an acetic acid-water mixture at elevated temperature for a designated time. When the heating process is completed, the metal solution is partially neutralized to a designated pH value using Na₂CO₃. The linker solution is prepared by co-dissolving 2-ATA and NaOH in DI water. The metal solution and the linker solution are mixed under vigorous stirring, and the formed UiO-66-NH₂ is separated from the mixture by filtration or centrifugation. The obtained crude UiO-66-NH₂ is washed with a dilute sodium hydroxide solution and DI water to remove any residual 2-ATA linker, sodium acetate and acetic acid. The production

of UiO-66-NH₂ is described in further detail (e.g., reactant mass, reaction conditions and product yield) in the Supporting Information (Page 4-5).

The processes described above are mostly on the lab scale, yet they will serve as the basis for the scaling up production of UiO-66-NH₂ to the pilot scale. In scaling up the process, the differences between the pilot-scale productions and the lab-scale productions (e.g., solvent recovery, reaction medium reuse, and heating methods) need to be properly accounted for. Hence, several assumptions were made, according to the chemical engineering design criteria, for the scale up process [57, 58], and these assumptions were introduced and discussed in detail in the Supporting Information. The final material and energy inputs for the hypothetical pilot-scale production of UiO-66-NH₂ were summarized in Table S3 through Table S8, and those values were used in conjunction with other data (e.g., life cycle impact data and market prices) in LCA and TEA calculations.

2.2 Life cycle Assessment

Life cycle assessment (LCA) is an environmental accounting tool that evaluates the environmental impacts of products, processes, and systems. LCA was performed following the steps defined by ISO 14040 [67], including goal and scope, inventory analysis, impact assessment, and interpretation. In this section, a detailed environmental assessment of UiO-66-NH₂ production via the conventional solvothermal system and the aqueous solution-based system was conducted based on the framework displayed in Figure 2.

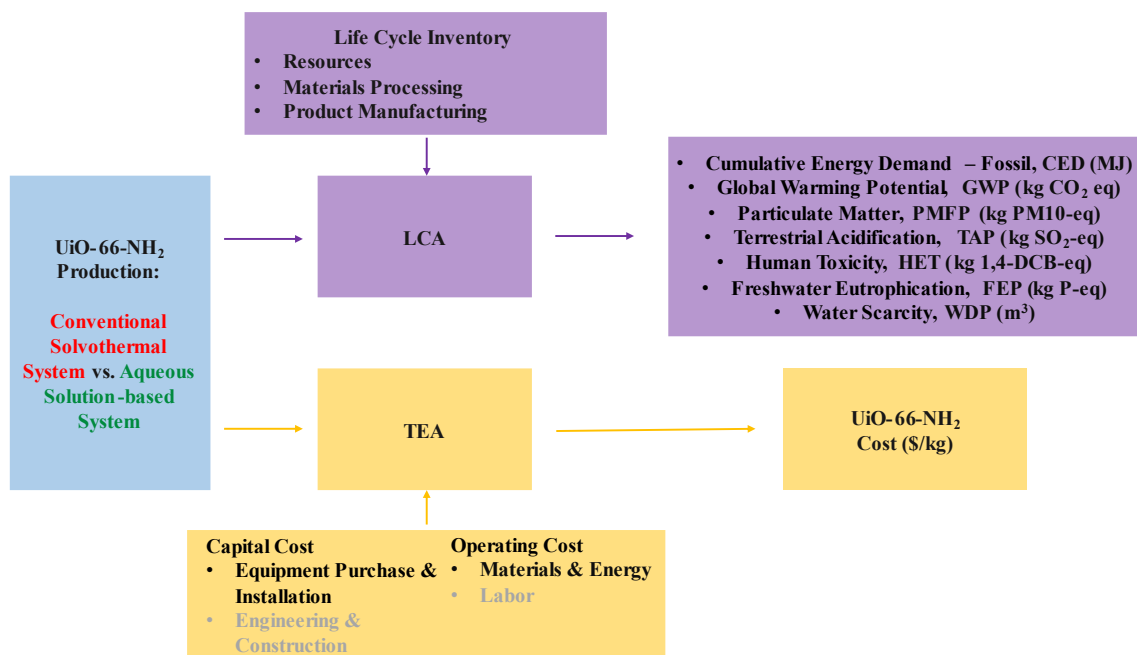


Figure 2. Representation of the overall LCA and TEA framework. In this study, a cradle-to-gate type LCA was carried out, and seven metrics were chosen to estimate the environmental impacts associated with the UiO-66-NH₂ production via both the solvothermal system and the aqueous solution-based system. The production cost of UiO-66-NH₂ from both systems was estimated by TEA. However, the labor costs and engineering construction cost (shaded in grey) were not accounted for in TEA due to their large regional variability and uncertainty.

2.2.1 Goal and scope

The goal of LCA in this study is first to analyze and understand the environmental burdens associated with UiO-66-NH₂ production via the conventional solvothermal system and the aqueous solution-based system and find the most environmentally friendly production route. We focused on the evaluation of environmental impacts of UiO-66-NH₂ production, while its utilization and end of life were not considered. Therefore, a cradle-to-gate scope of LCA was chosen. The system boundary comprised the chemical and energy consumptions associated with the raw material extraction and processing for UiO-66-NH₂ production. To compare the environmental impacts of the two production systems, a function unit (FU)

needed to be designated first. A mass-based FU was suitable in this study as it revealed the relationships between the production environmental impacts (e.g., GWP) and the production outcome (e.g., the mass of UiO-66-NH₂) [53, 68]. As such, the FU was selected to be 1 kg of UiO-66-NH₂ on a dry basis.

2.2.2 Life Cycle Inventory

The life cycle inventory (LCI) is a critical step in LCA as it creates the full inventory of the input/output of the target process. In this work, the LCI was created based on the chemical consumptions, the energy calculations, and the important assumptions for process scaling up. All these pieces of information were documented in the Supporting Information (Page 6-12), and some of the key information was provided below.

Chemical and pharmaceutical industries minimize solvent consumption for conventional solvothermal systems by recycling organic solvents at a rate of 90% by vacuum/ambient pressure distillation [46]; therefore, we adapted this technique in our analysis to ensure the economic feasibility and environmental favorability of the system [46]. We also assumed the washing step in the conventional solvothermal systems could be done with either methanol (route 1) or water (route 2). As such, three production routes were defined and evaluated in this work, including route 1, solvothermal system with methanol for cleaning; route 2, solvothermal system with DI water for cleaning; and route 3, aqueous solution-based system. Analyzing these three routes can reveal the change in the environmental favorability and economic feasibility of the UiO-66-NH₂ production when organic solvents are partially or fully replaced by water.

Since no information on the UiO-66-NH₂ production beyond lab-scale is available, the chemical consumptions were estimated from the corresponding lab-scale data, presented in Table S1 and S2, using the stoichiometric relationship and the limiting reactant-to-product yield. However, the definition of “yield” is somewhat ambiguous in literature [33]. Traditionally, researchers assume the percentage yield is identical to the percentage conversion of the limiting reactant, regardless of the percentage crystallinity of the

obtained MOFs. Alternatively, the percentage yield could be taken as the product of the percentage conversion of the limiting reactant and the percentage crystallinity of the MOFs. This alternative definition is more conservative, as it assumes the crystalline MOFs are the desired product. In this work, we assessed the environmental impacts of UiO-66-NH₂ production based on three scenarios: 1) the yield is the conversion rate regardless of crystallinity (mass-based FU); 2) yield is the product of conversion rate and crystallinity (crystallinity-based FU), which will eventually translate into the maximum process environmental impacts; and 3) yield is 100% (ideal case), which will eventually translate into the ideal minimum process environmental impacts.

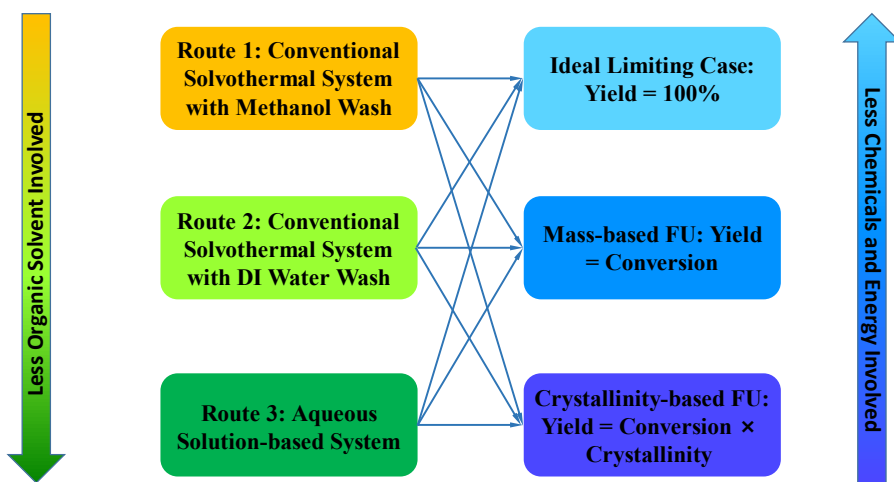


Figure 3. Illustration of the nine scenarios considered in this work.

In summary, three production routes were defined, and three yield definitions were used for each yield (Figure 3). These nine scenarios could represent a possible and reasonable range of the environmental burdens associated with the UiO-66-NH₂ production. In the main text, we focused our discussions on the mass-based FU, and the corresponding LCI data were summarized in Table 1 (combined from Table S5,

S6 and S13). Linear calculations were performed to convert these inventory data to crystallinity-based FU and ideal case (yield = 100%), and the full life cycle inventories for other FU cases could be found in Table S3, S4, S7, S8 (chemical consumptions and heat), and S13 (electricity).

Table 1. Summary of the materials and energy input for the conventional solvothermal and aqueous production of 1 kg UiO-66-NH₂ (mass-based FU) after scaling up. The products yield corresponding to this FU are 38% and 96% for the conventional solvothermal system and the aqueous solution-based system, respectively.

		Material/Energy	Solvothermal	Aqueous	
Zr	Precursor	Input			
		Production			
		ZrSiO ₄ (kg)	1.878	0.825	
		C (kg)	0.250	0.110	
		Cl ₂ (kg)	4.694	2.063	
		HCl (kg)	-	0.149	
		Water (kg)	-	2.984	
		Energy consumption			
		Heat (MJ)	6.668	5.24	
		Output			
		ZrCl ₄ (kg)	2.150	-	
		ZrOCl ₂ ·8H ₂ O (kg)	-	1.176	
		Linker Production	Input		
		(Nitration of TPA)	TPA (kg)	4.895	1.404
	H ₂ SO ₄ (kg)	7.995	2.293		
	HNO ₃ (kg)	2.092	0.832		
	Water (kg)	2.060	0.591		
	Energy consumption				
	Heat (MJ)	18.702	5.363		
	Electricity (kWh)	6.414	6.405		
	Output				
	2-NTA (kg)	4.479	1.285		

Linker Production	Input			
(Hydrogenation of 2-NTA)	2-NTA (kg)	4.479	1.285	
	NaOH (kg)	1.697	0.487	
	H ₂ (kg)	0.116	0.033	
	Pd/C (kg)	0.053	0.015	
	HCl (kg)	1.549	0.444	
	Water (kg)	108.758	31.190	
	Energy consumption			
	Heat (MJ)	7.503	2.152	
	Electricity (kWh)	6.733	6.496	
	Output			
2-ATA (kg)	2.305	0.661		
UiO-66-NH₂ Synthesis	Input			
2-ATA (kg)	2.305	0.661		
ZrCl ₄ (kg)	2.150	-		
HCl (kg)	7.368	-		
Water (route 1) (kg)	13.099	-		
Water (route 2) (kg)	787.093	-		
Water (route 3) (kg)	-	138.767		
DMF (kg)	24.355	-		
MeOH (route 1) (kg)	61.300	-		
ZrOCl ₂ ·8H ₂ O (kg)		1.176		
AcOH (kg)	-	4.793		
NaOH (kg)	-	0.347		
Na ₂ CO ₃ (kg)	-	1.210		
Energy consumption				
Heat (route 1) (MJ)	1182.227			
Heat (route 2) (MJ)	296.044			
Heat (route 3) (MJ)	-	6.946		
Electricity (kWh)	8.939	6.411		
Output				
UiO-66-NH ₂ (kg)	1	1		

2.2.3 Life cycle impact modeling

LCA was conducted using Excel spreadsheet and Econivent v3.6 database [59]. Cumulative energy demand - fossil (MJ), global warming potential (kg CO₂-Eq), particulate matter (kg PM₁₀-Eq), terrestrial acidification (kg SO₂-Eq), freshwater eutrophication (kg P-Eq), human toxicity (kg 1,4-DCB-Eq), and water scarcity (m³) were chosen as the metrics to evaluate the environmental impacts of the two UiO-66-NH₂ production systems (three routes) [69]. Cumulative energy demand and ReCiPe Midpoint method were used to calculate the life cycle environmental impacts mentioned above [70].

2.3 Techno-economic assessment

Techno-economic assessment was conducted to assess the total cost of producing 1 kg UiO-66-NH₂ via the conventional solvothermal system and the aqueous solution-based system. The total cost can be broadly categorized into the operating cost and the capital cost (Figure 2). Operating cost is comprised of the chemicals and energy consumption required for UiO-66-NH₂ productions. We collected the minimum, average, and maximum market price of chemicals from commercial selling websites, and these data were summarized in Table S9. The market price of electricity and natural gas was 0.0682 \$/kWh [47] and \$0.004/MJ [71], which stands for the average market price in the United States. The operating cost were then calculated by multiplying the chemical/energy consumption (Table 1) and their corresponding market price (Table S9). The capital costs were also assessed, and detailed information can be found in the Supporting Information (Table S11). It should be noted that the labor costs and engineering construction (shaded in grey in Figure 2) were not accounted for in this analysis due to their large regional variability and uncertainty. Finally, the total cost for UiO-66-NH₂ productions via different routes were calculated by summing operating costs and capital costs per FU.

Due to the variability associated with market price and process parameters (e.g., solvent recycle rate, MOF yield, etc.), we used a Monte Carlo simulation to quantify the effects of uncertainty. Monte Carlo simulation was conducted in the “R environment” for 10,000 trials. In each trial, values for variables were

randomly drawn from the defined distribution (triangular distribution, Table S14), and the aggregated results were used to produce probability distributions of the production costs for producing 1 kg UiO-66-NH₂ from three routes. In addition, a sensitivity analysis of UiO-66-NH₂ production costs from three routes was performed by varying one input parameter to its minimum value or maximum value while keeping other parameters at the baseline values (Table S14). The most sensitive parameters are the ones with the largest relative differences in production costs.

3. Result and discussion

3.1 Life cycle assessment

Cumulative energy demand (CED, MJ), climate change (GWP, kg CO₂ eq), particulate matter formation (PMFP, kg PM10-eq), terrestrial acidification (TAP, kg SO₂-eq), human toxicity (HTP, kg 1,4-DCB-eq), freshwater eutrophication (FEP, kg P-eq), and water depletion (WDP, m³) were evaluated for the UiO-66-NH₂ production via three routes. Before looking at the full life cycle of UiO-66-NH₂ production, we first examined the environmental impacts associated with the Zr precursor manufacturing. The relative impacts of producing 1 kg of Zr precursor (e.g., ZrCl₄ and ZrOCl₂·8H₂O) as well as the percentage contribution of each input are presented in Figure 4.

As shown in Figure 4(a), ZrCl₄ has relatively higher environmental burdens than ZrOCl₂·8H₂O under all metrics other than HTP. This observation might be counterintuitive since ZrOCl₂·8H₂O is produced from ZrCl₄, and additional chemicals and energy are used in the ZrOCl₂·8H₂O manufacturing. However, the molar conversion of ZrCl₄ to ZrOCl₂·8H₂O is high (90%), and the molar mass of ZrOCl₂·8H₂O (322 g/mol) is also much higher than that of ZrCl₄ (233 g/mol). Accordingly, 1 kg of ZrCl₄ could yield 1.244 kg of ZrOCl₂·8H₂O, and such 24% mass gain eventually led to lower environmental burdens (except for HTP) associated with ZrOCl₂·8H₂O since all the metrics are per mass-based.

The overall impacts of producing 1 kg of Zr precursor was further itemized to investigate the contribution of each input, and the results are shown in Figure 4(b) (ZrCl₄) and Figure 4(c) (ZrOCl₂·8H₂O).

In general, the environmental impacts associated with the $ZrCl_4$ manufacturing and the $ZrOCl_2 \cdot 8H_2O$ manufacturing have a highly similar structure, and the Zr resource, zircon, is the dominating factor that accounts for 66% to 100% of the total environmental impacts in all metrics other than HTP. This observation, that an inorganic precursor (e.g., $ZrCl_4$) has similar environmental impacts as its first-generation source (e.g., zircon), will be further discussed quantitatively later. As for the HTP metric, its environmental burdens are mainly attributed to the reagent consumption (e.g., HCl and Cl_2). Despite the highly similar environmental impacts structure, certain differences exist in the GWP metric, the CED metric and the HTP metric between the $ZrCl_4$ manufacturing and the $ZrOCl_2 \cdot 8H_2O$ manufacturing. Compared to $ZrCl_4$, reagents and energy associated $ZrOCl_2 \cdot 8H_2O$ manufacturing has slightly higher shares in GWP, CED and HTP. This observation could be explained from the use of extra material (i.e., HCl) and heat in the conversion of $ZrCl_4$ into $ZrOCl_2 \cdot 8H_2O$, which have slight impacts on GWP, CED and HTP. Meanwhile, the use of extra material and heat has negligible impacts on other metrics; therefore, the percentage contribution of each input is identical for those metrics.

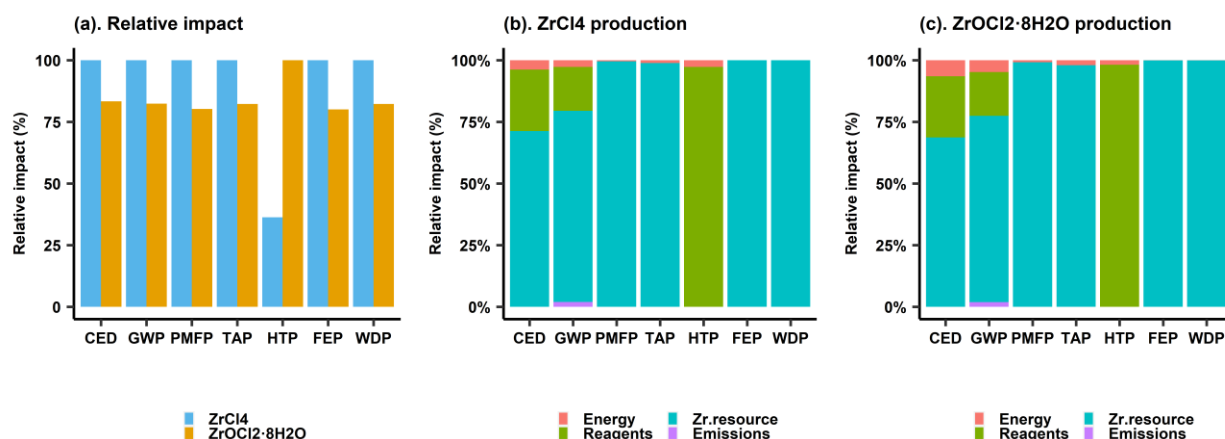


Figure 4. Relative environmental impacts of Zr precursor productions (a) and their breakdown for $ZrCl_4$ (b) and $ZrOCl_2 \cdot 8H_2O$ (c). Chemicals other than the Zr source are merged as “Reagents” in the plot.

The environmental burdens associated with three routes were evaluated, including (1) conventional solvothermal system with methanol wash; (2) conventional solvothermal system with water wash; and (3) aqueous solution-based system. To better understand the effects of yield definition on the environmental impacts of UiO-66-NH₂ production, we computed the results of each route based on the mass-based FU, the crystallinity-based FU, and the ideal case. The product yield associated with mass-based FU, crystallinity-based FU and ideal case are [36%,96%], [18%,38%], and [100%,100%] for the solvothermal system (route 1 and 2) and the aqueous solution-based system (route 3), respectively. For all metrics, the higher the percentage value or absolute value, the greater environmental burdens associated with UiO-66-NH₂ production are. A comparison between the relative environmental impacts of producing 1 kg UiO-66-NH₂ via the three routes is presented in Figure 5, and the absolute value of the environmental impacts is shown in Figure S1. The results in Figure S1 suggest the absolute environmental burdens associated with UiO-66-NH₂ production increase monotonically with the decreasing product yield, regardless of the choice of production route. This observation is not surprising, as more chemicals and energy are supposed to be consumed at lower product yield, leading to higher environmental burdens. The results in Figure 5 reveal that route 1 has the highest environmental burdens for metric, route 3 has the lowest environmental burdens, and the environmental burdens of route 2 lies in between. This observation holds true for the mass-based FU, the crystallinity-based FU and the ideal case. Our discussion in the following section will be mainly based on mass-based FU, i.e., the results in Figure 5 (a), unless otherwise specified, and we believe the conclusions drawn below hold true for the other two FUs.

As shown in Figure 5(a), the environmental burdens of route 1 are higher than those of route 2 in all metrics, and the differences in environmental burdens are very prominent (greater than 25%) in CED, GWP, and TAP. The major process difference between route 1 and route 2 is the choice of washing agent (methanol for route 1 and water for route 2). Methanol is reported to have considerably higher carbon intensity, energy intensity, and terrestrial acidification intensity (1.46 kg CO₂ eq/kg , 43.7 MJ/kg, and 0.0012 kg SO₂-eq/kg) [59] when compared to water. Consequently, we observe considerable reductions (up

to 50%) in CED, GWP, and TAP but marginal changes in the remaining categories by switching the washing agent from methanol to water.

The environmental burdens of UiO-66-NH₂ production are readily alleviated by simply replacing the organic washing agent with water, and a much better environmental performance is achieved by completely eliminating the organic solvents in the production. We did a further comparison between route 1 and route 3 and found significant reductions (up to 91%) on all the environmental metrics when using the aqueous solution-based system (route 3). Such observation can be explained from two aspects. First, the use of the aqueous solution-based system completely eliminates the consumption of organic solvents. Organic solvents, especially DMF, have high environmental burdens in most metrics evaluated in this work. Replacing these organic solvents with water in the UiO-66-NH₂ production completely eliminates their environmental burdens. Next, higher product yield was achieved when using the aqueous solution-based system. Compared with the conventional solvothermal system, the aqueous solution-based system has a product yield of 96% (on mass-based FU) and 36% (on crystallinity-based FU), which is 2-3 times higher than the product yield from the conventional solvothermal system. Higher production yield eventually translates into lower chemical consumptions, which leads to lower environmental burdens. To say the least, even if the product yield is 100% for both systems, which represents the ideal case for both systems, the aqueous solution-based system still has the lowest environmental impacts in all metrics.

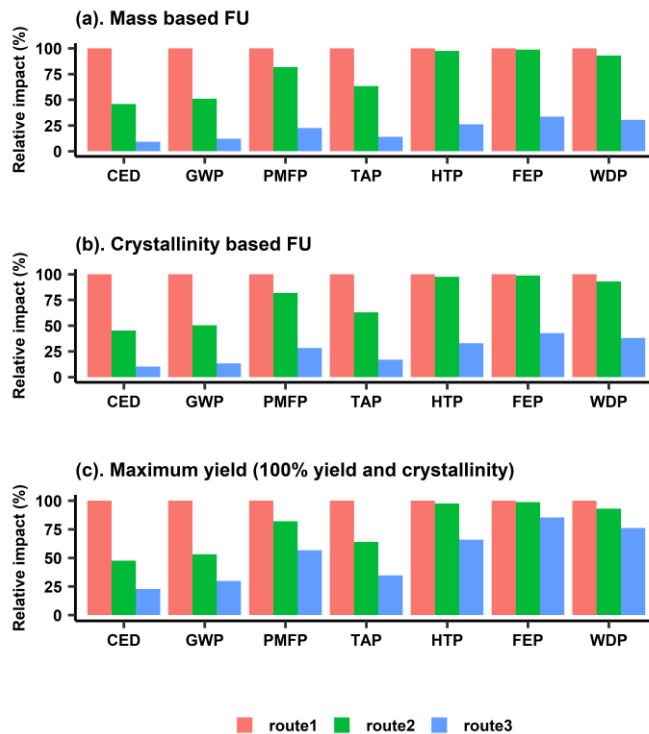


Figure 5. Relative environmental impacts of route 1, conventional solvothermal with methanol for cleaning; route 2, conventional solvothermal system with water for cleaning; and route 3, rapid aqueous system with water for cleaning. Mass based FU, crystallinity-based FU, and maximum yield correspond to product yield of [38%, 18%, 100%] and [96%, 36%, 100%] for the solvothermal system (route 1 and 2) and the aqueous solution-based system (route 3), respectively. Absolute values are available in Figure S1.

Similar to the analysis in Figure 4(b) and (c), the overall relative environmental impacts in Figure 5 were itemized to identify the contributions of each input to every environmental metric, and the results are shown in Figure 6. In general, the environmental impacts associated with route 1 and route 2 have a similar structure, so route 1 and route 2 will be discussed together first. In both route 1 and route 2, the organic solvents, DMF and methanol, are the major or dominating contributor to all the environmental metrics, despite the high recycling rate (90%) assumed for the solvothermal system. In other words, if the DMF and methanol recycle is not considered, as was done in some other works [53], these two organic solvents would possibly contribute to almost 100% of the total environmental impacts of UiO-66-NH₂

production. Beside DMF and methanol, heat has considerable impacts on CED, GWP, PMFM, and TAP, and those impacts are more prominent in route 1 compared to route 2. This observation could be explained from two aspects. On the one hand, heat was assumed to be generated by the natural gas combustion, which has major impacts on CED, GWP, PMFM, and TAP. On the other hand, a large amount of extra heat, as will be discussed later, was required for the methanol recycle in route 1. Compared to the organic solvents and heat, reagents, linker, and Zr precursors have less significant impacts on GWP and CED (less than 20%) but considerable impacts on the remaining metrics. Finally, electricity has negligible impacts on all the categories for the solvothermal system. The environmental impact structure of route 3 is significantly different from that of route 1 or route 2. In route 3, reagents, linker, and Zr precursors have the major shares across all the environmental categories, and together they account for 90-100% of the impacts. Electricity and heat have minor to negligible impacts on all the categories. The results from Figure 6 suggest that, as the UiO-66-NH₂ production is shifted from the conventional solvothermal system to the aqueous solution-based system, the environmental burdens associated with the production are approaching their minimum values, i.e., the limit set by the chemicals.

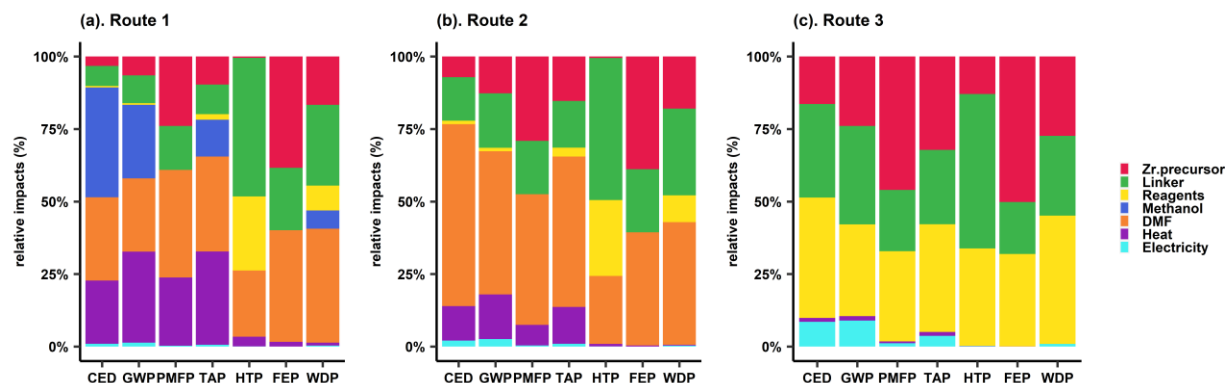


Figure 6. Breakdown of the relative environmental impacts of producing 1 kg UiO-66-NH₂ via route 1, 2, and 3. Chemicals other than the Zr precursors and the linker are merged as “Reagents” in the plot.

Among all the environmental metrics studied in Figure 4 through Figure 6, CED and GWP are often regarded as the most important metrics since the energy and climate change performances usually gain the most attention in practical chemical productions [72]. As such, the GWP and CED data were plotted with their absolute values in Figure 7 to help understand the energy and climate change performances of the Zr precursor production and the UiO-66-NH₂ production. As shown in Figure 7(a) and (c), the GWP and CED associated with the two Zr precursors, ZrOCl₂·8H₂O and ZrCl₄, are comparable, and both precursors have 9-10 kg CO₂ eq/kg GWP and 90-100 MJ/kg CED. The GWP and CED values of the two Zr precursors are not significantly different from those for the Zr source (zircon), which has a 9.4 kg CO₂ eq/kg GWP and an 87.7 MJ/kg CED. The inorganic precursors (ZrOCl₂·8H₂O and ZrCl₄) have comparable GWP and CED as their first-generation source (zircon), which is likely due to the fact that only inorganic reagents (e.g., Cl₂ and HCl) were used in the precursor manufacturing and these reagents have minor impacts on the GWP and CED. Similar results were reported in other literature that estimated the GWP and CED of different metal precursor (e.g., Ti salt) for nanoparticle synthesis [68, 72]. To the best of our knowledge, few studies on the life cycle impact assessment of different Zr precursors have been conducted, yet we expect a growing need for this analysis as more studies might be done in the future to evaluate the life cycle environmental performances of other Zr-based MOFs/materials. The values calculated in this work could be used when ZrCl₄ or ZrOCl₂·8H₂O is used to produce UiO-66 derivatives or ZrO₂. When other Zr precursors were to be used, perhaps the data for zircon could be used as a first pass approximation, if no organic reagent is used in the precursor manufacturing. However, if organic reagents are consumed, the manufacturing process needs to be analyzed to get those data, and examples were provided in the Supporting Information of this work.

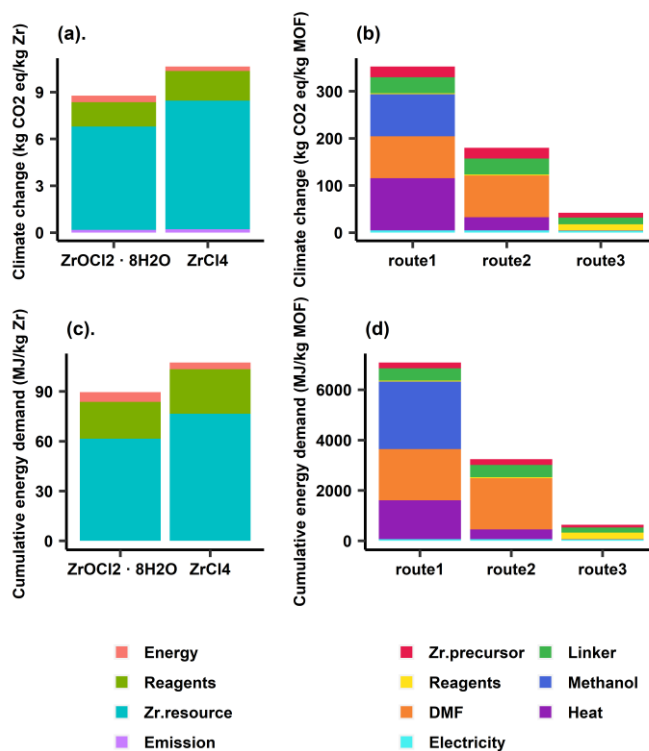


Figure 7. Global warming potential (kg CO₂ eq) for producing (a) 1 kg of Zr precursors and (b) 1 kg of UiO-66-NH₂ and Cumulative energy demand (MJ) for producing (c) 1 kg of Zr precursors and (d) 1 kg of UiO-66-NH₂ (on mass basis). The definition of “Reagents” can be found in Figure 4 and 6.

In the UiO-66-NH₂ production (Figure 7(b) and (d)), the GWP and CED associated with route 1, 2, and 3 are 353, 180, and 43 kg CO₂ eq/kg, and 7080, 3244, and 649 MJ/kg, respectively. For both route 1 and route 2, the same amount of DMF was used and the heat required for DMF recycle is the same. The difference in GWP and CED between route 1 and route 2 came from the methanol consumption and the heat for methanol regeneration. In route 1, 61.3 kg of methanol was assumed to be consumed in the cleaning process, and such consumption eventually translated into a CED of 2677 MJ (energy intensity of 43.7 MJ/kg) and a GWP of 89 kg CO₂ eq (carbon intensity of 1.46 kg CO₂ eq/kg) per 1 kg UiO-66-NH₂. Besides methanol, route 1 requires a significant amount of heat to power the organic solvent recovery process. It is estimated that 1182 MJ of heat was consumed, and this amount of heat corresponds to a CED of 1577 MJ (energy

intensity of 1.3MJ/MJ) and a GWP of 113 kg CO₂ eq (carbon intensity of 0.094 kg CO₂ eq/kg). By replacing the solvothermal system with the aqueous solution-based system, a substantial reduction of both GWP and CED, up to 88% and 91 %, was observed. The quantitative analysis results here further emphasized the superior environmental performance of the aqueous solution-based system in UiO-66-NH₂ production. If the organic solvents are essential for the synthesis of other MOFs (i.e., if certain chemistry does not work in water), then the following ideas could be considered to alleviate the environmental burdens of the production: (1) replacing the organic solvent with water in the washing step; and (2) recycle/reuse as much organic solvent as possible from the washing step if water cannot be used for cleaning purposes (e.g., HKUST-1 degrades in water over time[73]).

The LCA results in this work are in good agreement with results reported by Grande *et al.* Their study suggested the climate change impacts of producing CPO-27-Ni decreased by two orders of magnitude (from 1136.2 to 12.3 kg CO₂ eq) when an all water-based synthesis and cleaning process was used [53]. However, the results from their study were based on the laboratory-scale batches, where the reutilization of organic solvents and other chemicals were not optimized. Our analysis accounted for the solvent recovery (recycle rate of 90%) and the corresponding energy requirement, so our results are possibly more representative for the pilot/large scale UiO-66-NH₂ production (and perhaps other MOFs production). In summary, our results highlight the high environmental favorability of the aqueous solution-based system in the production of UiO-66-NH₂, and we expect similar outcomes in the production of other MOFs where an aqueous-solution based system could be used.

3.2 Techno-economic assessment

The economic profitability of different UiO-66-NH₂ production routes is evaluated by TEA. In TEA, the major metric is the production cost (Figure 8), i.e., the minimum selling price of UiO-66-NH₂ that makes the production breakeven. A breakdown of the production cost (Figure 9) and sensitivity analysis (Figure 10) is also provided.

As mentioned earlier, Monte Carlo simulation was used to account for the variability associated with market price and process parameters, and the simulated production cost distributions for route 1, 2, and 3 on the mass-based FU are displayed in Figure 8(a), (b) and (c), respectively. Across the uncertainty range (e.g., market price, solvent recovery rate, yield, etc.) defined in Table S14, route 1 has the highest mean production cost (98 \$/kg), with 90% of results from 78 \$/kg to 117 \$/kg. The average production cost of route 2 (66 \$/kg) is slightly lower than that of route 1, with 90% of outcomes from 56 \$/kg to 78 \$/kg. Finally, route 3 has the lowest average production cost (15.8 \$/kg), with 90% of outcomes from 14.2 \$/kg to 17.5 \$/kg. The simulated production cost distributions for route 1, 2, and 3 on crystallinity-based FU and for the ideal case are presented in Figure S2 and Figure S3. The mean values of production costs for route 1, 2, and 3 are found to be 196 \$/kg, 131 \$/kg, and 33.8 \$/kg for the crystallinity-based FU, and 44 \$/kg, 32 \$/kg, and 15.5 \$/kg for the ideal case. The economic analysis suggests that, in addition to the superior environmental favorability, the aqueous solution-based system is also much more economically feasible in UiO-66-NH₂ production compared to the conventional solvothermal system, regardless of the yield definition. This result is in good agreement with some of the previous TEA studies on other MOFs. For example, DeSantis *et al.* conducted TEA on several MOF adsorbents, including Mg₂(dobdc), Ni₂(dobdc), HKUST-1 (H₃btc), and MOF-5 (H₂bdc). In their study, significant cost reduction (34-83% reduction) was achieved by replacing the solvothermal synthesis with liquid assisted grinding synthesis or aqueous synthesis [46]. The production cost of UiO-66-NH₂ from the aqueous solution-based system (15.8 \$/kg) is comparable to that of Ni and Mg-based MOFs estimated by DeSantis *et al.* (10-20 \$/kg for aqueous synthesis, [yield = 92%]), yet the production cost of UiO-66-NH₂ from the solvothermal system (62 \$/kg to 110 \$/kg) evaluated in our study is higher than the results from DeSantis *et al.* (35 \$/kg to 71 \$/kg). We attributed the higher production cost for the solvothermal system to the low UiO-66-NH₂ yield (38% ± 4%) used in this study, as opposed to the higher product yield (44% - 69%) used by DeSantis *et al.* If the UiO-66-NH₂ yield from the solvothermal system is comparable to the yield of those Ni/Mg-based MOFs, then the production cost should be similar.

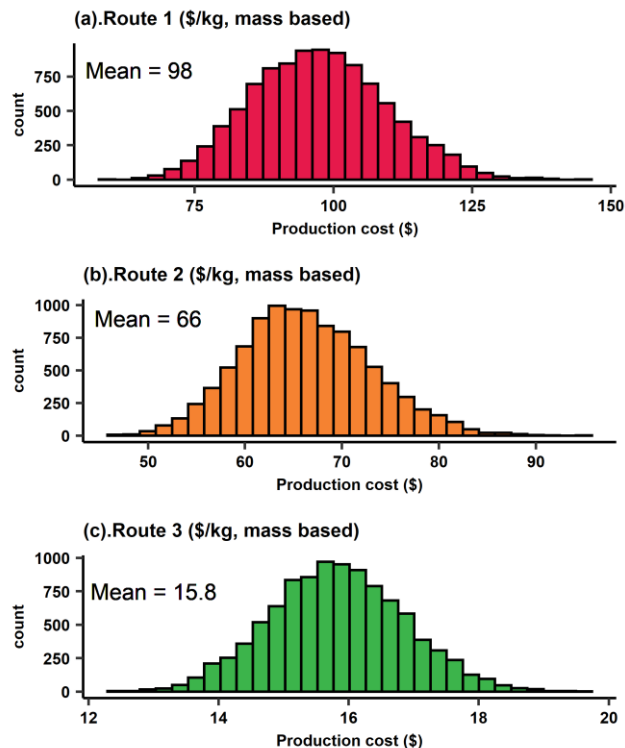


Figure 8. Production cost distributions of UiO-66-NH₂ on mass basis for (a) route 1, (b) route 2 and (c) route 3.

The detailed breakdown of the production cost for UiO-66-NH₂ via route 1, 2, and 3 is displayed in Figure 9. The total cost can be broadly categorized into the operating cost and the capital cost (Figure 2). The operating cost includes the raw chemicals for linker production, the Zr precursors, other reagents (e.g., HCl), organic solvents (i.e., methanol and DMF), water, and energy consumption (i.e., heat and electricity). The capital cost is taken as the purchasing and installation cost of all pieces of equipment in the project lifetime. Similar to the breakdown of environmental impacts in Figure 6, route 1 and route 2 have a similar structure for their total cost, and operating cost is the major contributor, accounting for 82% of the total cost for route 1 and 75% for route 2, respectively. In particular, organic solvents have significant impacts on the operating cost, contributing to 47 \$/kg (59%) and \$26/kg (43%) of the operating cost for route 1 and

2, respectively. Again, the main difference between the production cost of route 1 and route 2 (i.e., 31 \$/kg difference) came from the consumption of methanol and the use of extra heat in methanol recovery, while other parameters are almost identical between the two routes. Such observation reveals the economic favorability of using water as the cleaning agent, even in the solvothermal system. In the aqueous solution-based system, the equipment and linker cost became the major contributor to the total costs, accounting for 5.4 \$/kg and 5.7 \$/kg of the total cost, respectively. The remaining total cost is shared by other chemicals and energy. Compared to route 1 or route 2, a significant cost reduction (up to 84%) is achieved for route 3. Such observation can be explained from both the operating cost aspect and the capital cost aspect. On the operating cost aspect, the aqueous solution-based system completely eliminates the use of expensive organic solvents, leading to a substantial reduction in terms of the production financial burdens. Additionally, the high UiO-66-NH₂ yield in the aqueous solution-based system allows for lower linker consumptions compared to the solvothermal system (Table 1), so therefore the cost for linkers is also minimized (5.7 \$/kg in route 3 vs. 19 \$/kg in route 1 and route 2). On the capital cost aspect, the cost for the aqueous-solution based system is only one third of that for the solvothermal system, i.e., 5.4 \$/kg vs. 17.4 \$/kg. This significant saving on the capital cost is a direct outcome of the high STY nature of the aqueous solution-based system in UiO-66-NH₂ production. On the one hand, the precursor concentration in the aqueous solution-based system is much higher than that in the solvothermal system, so the required reactor volume per kg UiO-66-NH₂ is greatly reduced such that the total equipment purchasing cost is reduced. On the other hand, the shortened production time, i.e., 2 hrs in the aqueous solution-based system vs. 24 hrs in the solvothermal system, allows the same production line to produce more batches of UiO-66-NH₂ in its life time, which also reduces the capital cost per FU. It should be noted that we made a rather conservative assumption on the production rate of the aqueous solution-based system (3 batches per day), but this assumption could be relaxed if further evidence supports a higher production rate. In that case, the capital cost associated with the aqueous solution-based system could be further reduced, and route 3 will become more economically favorable. The results from Figure 9 suggest that, as the UiO-66-NH₂ production is shifted from the conventional solvothermal system to the aqueous solution-based system, the

production economic favorability greatly increased from both the operating cost aspect and the capital cost aspect.

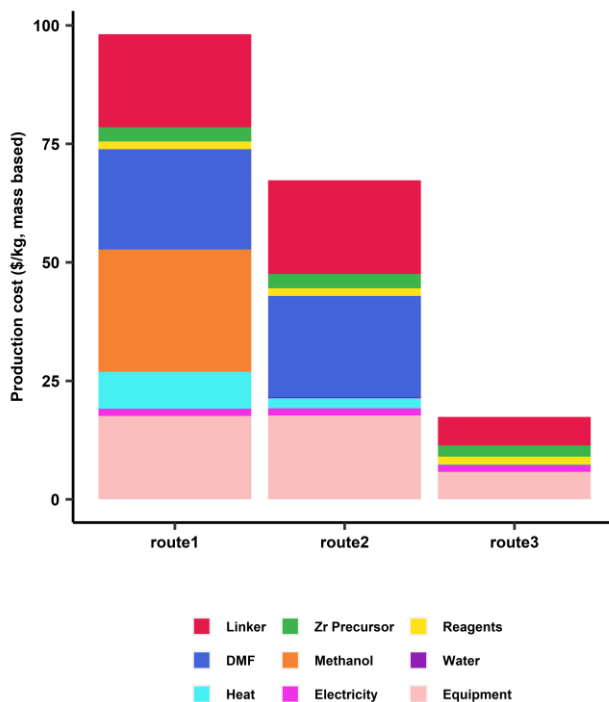


Figure 9. Breakdown of the UiO-66-NH₂ production cost (mass-based FU). The definition of “Reagents” can be found in Figure 6.

Finally, a sensitivity analysis was conducted to investigate the variability of key variables (Table S14) on the production cost, and the top four variables for each route were presented in Figure 10. For the solvothermal system, the organic solvent recycle rate is the most sensitive parameter, leading to large changes in production costs. Besides the solvent recycle rate, the market price of organic solvents (i.e., DMF and methanol) is also impactful. This is not surprising, as both solvents recycle rate and market price could directly translate into the solvent costs, which are found to be crucial for the production cost (Figure 9). Finally, the MOF yield is also an important variable for solvothermal systems, suggesting that future improvement in the synthesis method might reduce the production cost. As for the aqueous solution-based system, the linker yield and the market price of Pd/C are the most sensitive parameters. Such observation

is consistent with the production costs distribution (Figure 9), as the cost associated with linker production contributes to 36% of the total cost. The equipment capital costs and equipment lifetime also have appreciable impacts on the production costs, demonstrating that extension of the equipment lifetime and reduction of the capital costs will be effective methods to reduce the production costs of the aqueous system.

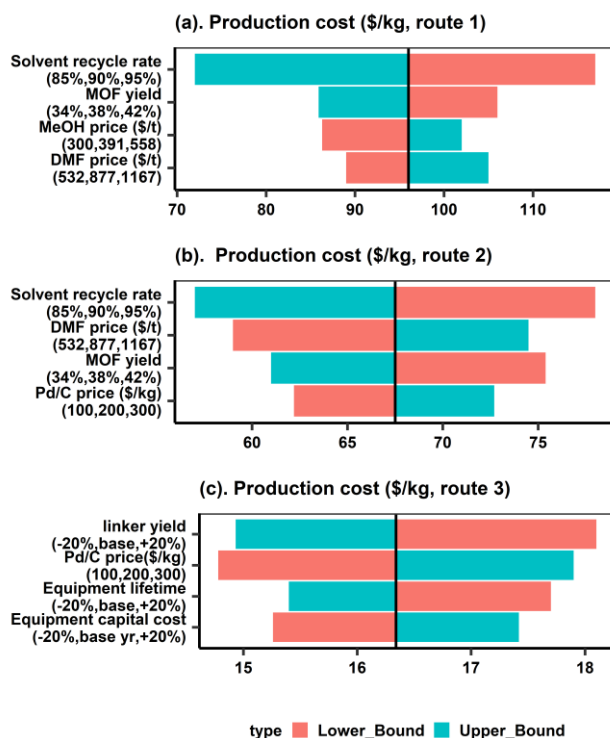


Figure 10. Sensitivity analysis of production costs (mass-based FU).

Our TEA results highlight the high economic favorability of the aqueous solution-based system in the production of UiO-66-NH₂, and these results might extend to the aqueous solution-based production of other MOFs. Together with the LCA results in the previous section, we conclude that the aqueous solution-based production is the most environmentally friendly and economically favorable method of UiO-66-NH₂. In the next section, we will discuss some implications behind the sustainability-related applications of UiO-66-NH₂ based on our LCA-TEA results.

3.3 Environmental implications

Recently, UiO-66-NH₂ and other UiO-66 derivatives have attracted a lot of research interests in terms of CO₂ capture and storage [41, 45, 54-56, 74, 75], which is a promising route to achieve significant CO₂ reduction in the near term [76]. Both the UiO-66-NH₂ and other UiO-66 derivatives have good stability and moderate CO₂ uptakes, ranging from 60 g/kg to 260 g/kg [41-45, 54-56, 74, 75], therefore previous literature studies have regarded them as a promising tool to mitigate the greenhouse gas emissions [41-45, 54-56, 74, 75]. Such a conclusion might be true if we only look at the gate-to-grave part of the UiO-66-NH₂ life cycle. However, if the cradle-to-gate part of UiO-66-NH₂ life cycle is also included, i.e., if we consider the full life cycle of UiO-66-NH₂, the previous conclusion, that UiO-66-NH₂ is a promising tool to mitigate the GHG emissions, might be subverted, depending on how UiO-66-NH₂ is used in the CO₂ capture and separation. In the following discussions, we will assume the UiO-66-NH₂ is made from the most environmentally friendly route, the aqueous solution-based system, at the ideal yield (100%). Under this assumption, the GWP value of UiO-66-NH₂ is 42 kg CO₂ eq/kg.

In the simplest case, UiO-66-NH₂ is applied in a single-use manner, and the CO₂ saturated UiO-66-NH₂ is buried such that the adsorbed CO₂ is fixed. In this case, the life-cycle environmental benefit of UiO-66-NH₂ is -0.06 to -0.26 kg CO₂ eq/kg, and is negligible compared to its upstream life-cycle environmental burdens. Hence, if UiO-66-NH₂ is used in this manner, it is not a good candidate to mitigate GHG emissions, especially when comparing to other single-use negative emission technologies (e.g., biochar for carbon sequestration) [77, 78]. Alternatively, UiO-66-NH₂ could be used as an intermediate storage medium for CO₂ capture, i.e., UiO-66-NH₂ is used to concentrate CO₂, in post-combustion CO₂ capture and storage (CCS). In this case, UiO-66-NH₂ could be regenerated and reused, and its life-cycle environmental benefit might exceed its life-cycle environmental burdens. However, regenerating and reusing UiO-66-NH₂ does not guarantee that UiO-66-NH₂ is a better alternative than the current benchmark CCS medium, monoethanolamine (MEA) [79-81], because MEA has a higher CO₂ uptake (364-400 g/kg)[82, 83] and a much lower cradle-to-gate GWP (3.46 kg CO₂ eq/kg) [59]. Indeed, the solvent loss (0.0032 kg MEA/kg CO₂ captured) [76] and energy consumption (3-4 MJ/kg CO₂ captured) [84, 85]

associated with MEA regeneration can be concerning factors. It is possibly true that less energy demand and material loss can be achieved to regenerate UiO-66-NH₂ than MEA [86], yet further quantitative analysis is required to determine if the emission reduction in sorbent regeneration could overcome the higher emissions associated with upstream production before claiming UiO-66-NH₂ as a more sustainable alternative for MEA in CCS. Hence, we computed the total amount of CO₂ captured as a function of the number of CO₂ capture-solvent/sorbent regeneration cycles for both UiO-66-NH₂ and MEA (Figure 11) to compare their performances in post-combustion CCS. When the number of cycles is zero, the amount of CO₂ captured is -42 kg for UiO-66-NH₂ and -3.46 kg for MEA, and these values correspond to the cradle-to-gate emission of the two material. When the number of cycles is greater than zero, both UiO-66-NH₂ and MEA have a net positive amount of CO₂ captured per cycle (i.e., the amount of CO₂ captured is greater than the amount of CO₂ emissions associated with solvent/sorbent regeneration and replenishment), and they start to create a positive life-cycle CO₂ capture after 169-757 cycles (UiO-66-NH₂) or 13-16 cycles (MEA). Compared to UiO-66-NH₂, MEA achieve a positive life-cycle CO₂ capture much faster because it has higher CO₂ uptake and much lower cradle-to-gate GWP. When the number of cycles is greater than 1513, the life-cycle CO₂ capture of UiO-66-NH₂ starts to overlap with that of MEA (shaded area), suggesting UiO-66-NH₂ becomes a comparable/more sustainable alternative to MEA. In the future CCS studies involving UiO-66-NH₂ (or other UiO-66 derivatives), it is perhaps worth looking into the ways to use aqueous solution-based systems to produce UiO-66-NH₂ with higher CO₂ uptake, lower regeneration energy requirement, and elongated lifetime.

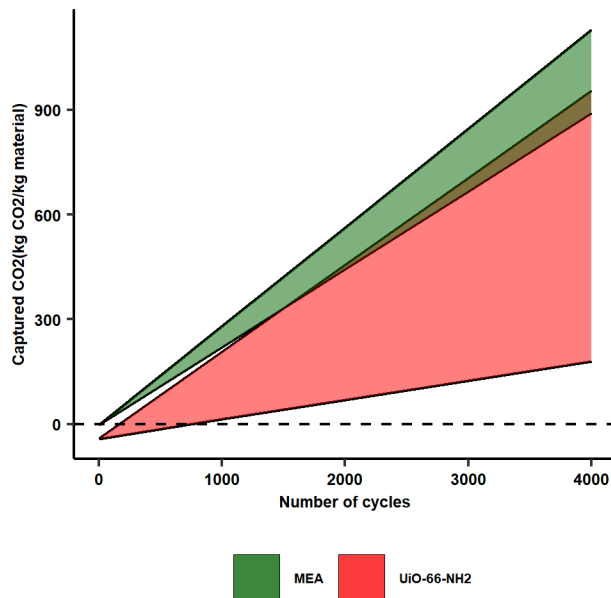


Figure 11. Comparison between the performance of MEA (green) and UiO-66-NH₂ (red) in post-combustion CCS. For MEA, the CO₂ uptake is 0.364-0.4 kg CO₂/kg solvent [82, 83], the heat of regeneration is 3-4 MJ/kg CO₂ captured [84, 85], and the solvent loss is 0.0032 kg MEA/kg CO₂ captured [76]. For UiO-66-NH₂, the CO₂ uptake is 0.06-0.26 kg CO₂/kg sorbent [41-45, 54-56, 74, 75], the heat of regeneration is assumed to be 20-35 kJ/mol CO₂ captured (identical to the heat of sorption) [86], and the sorbent loss is assumed to be zero due to the lack of data. The heat of regeneration is assumed to be supplied by natural gas combustion. The net amount of CO₂ captured per cycle is 0.056 kg (lower bound)/0.249 kg (upper bound) for UiO-66-NH₂ and 0.223 kg (lower bound)/0.283 kg (upper bound) for MEA, respectively.

The discussions above emphasized the importance of considering the cradle-to-gate impacts of UiO-66-NH₂ when it is used in sustainability-related applications. To date, a large variety of materials has been created and used for sustainable purposes, while most research efforts have been focused on gate-to-grave environmental impacts. For those materials, the cradle-to-gate LCA could be implemented to comprehensively evaluate the full life-cycle sustainability.

4. Conclusions

In this paper, process-based cradle-to-gate LCA and TEA were carried out to evaluate the life cycle environmental impacts and production costs associated with UiO-66-NH₂ production via the conventional solvothermal system and the aqueous solution-based system on the pilot-scale. The LCA results demonstrate that the aqueous solution-based system has much lower environmental impacts compared to the conventional solvothermal system. The aqueous solution-based system differs from the conventional solvothermal system by using water as the solvent and the cleaning agent. In this regard, the significant environmental burdens associated with organic solvents production and heat required for solvent recovery could be avoided. Furthermore, higher product yield is achieved in the aqueous solution-based system such that less material is consumed and the environmental burdens are lower. Compared with the solvothermal system, the aqueous solution-based system reduces the environmental impacts to up to 91%. A similar trend was observed in the TEA. The production cost of UiO-66-NH₂ from the aqueous solution-based system (14.2 \$/kg to 17.5 \$/kg) is much lower compared to that from the solvothermal system (62 \$/kg to 110 \$/kg) due to the significant reduction of operating costs.

Our results reveal UiO-66-NH₂ production from the aqueous solution-based system is significantly more environmentally and economically feasible than the solvothermal system, and we believe this conclusion holds true for other MOFs given the high contributions of organic solvent usage to TEA and LCA metrics. Despite the environment and economic favorability of aqueous system, if UiO-66-NH₂ is applied in sustainability-related areas (e.g., CO₂ capture and storage), further research should be done to investigate if UiO-66-NH₂ could be a better alternative to the existing benchmark (i.e., MEA) via comprehensive cradle-to-grave LCA. Given the high number of cycles required (~1500) for UiO-66-NH₂ to match the life-cycle CO₂ capture of MEA it is apparent there are remaining technical challenges for MOFs to be deployed at scale as an optimal material for CCS.

To the best of our knowledge, this work is the first LCA and TEA study on UiO-66-NH₂ production via different synthesis systems. The findings of this article help identify the most promising approaches for MOFs synthesis at scale. In particular, using aqueous synthesis approaches seems to be eco-friendlier and more cost-effective if possible.

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Authorship statement:

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Reference:

1. Furukawa, H., et al., *The chemistry and applications of metal-organic frameworks*. Science, 2013. **341**(6149).
2. Rowsell, J.L. and O.M. Yaghi, *Metal-organic frameworks: a new class of porous materials*. Microporous and mesoporous materials, 2004. **73**(1-2): p. 3-14.
3. Zhou, H.-C., J.R. Long, and O.M. Yaghi, *Introduction to Metal-Organic Frameworks*. Chemical Reviews, 2012. **112**(2): p. 673-674.
4. i Xamena, F.X.L., et al., *MOFs as catalysts: Activity, reusability and shape-selectivity of a Pd-containing MOF*. Journal of Catalysis, 2007. **250**(2): p. 294-298.
5. Lee, J., et al., *Metal-organic framework materials as catalysts*. Chemical Society Reviews, 2009. **38**(5): p. 1450-1459.
6. Wang, X., et al., *MOF derived catalysts for electrochemical oxygen reduction*. Journal of Materials Chemistry A, 2014. **2**(34): p. 14064-14070.
7. Dolgoplova, E.A., et al., *Photochemistry and photophysics of MOFs: steps towards MOF-based sensing enhancements*. Chemical Society Reviews, 2018. **47**(13): p. 4710-4728.
8. Kreno, L.E., et al., *Metal-organic framework materials as chemical sensors*. Chemical reviews, 2012. **112**(2): p. 1105-1125.
9. Liu, B., et al., *Four uncommon nanocage-based Ln-MOFs: highly selective luminescent sensing for Cu 2+ ions and selective CO 2 capture*. Chemical Communications, 2014. **50**(63): p. 8731-8734.

10. Legrand, A., et al., *Enhanced Ligand-Based Luminescence in Metal–Organic Framework Sensor*. ChemNanoMat, 2016. **2**(9): p. 866-872.
11. Dincă, M. and J.R. Long, *Hydrogen storage in microporous metal–organic frameworks with exposed metal sites*. Angewandte Chemie International Edition, 2008. **47**(36): p. 6766-6779.
12. Eddaoudi, M., et al., *Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage*. Science, 2002. **295**(5554): p. 469-472.
13. Furukawa, H. and O.M. Yaghi, *Storage of hydrogen, methane, and carbon dioxide in highly porous covalent organic frameworks for clean energy applications*. Journal of the American Chemical Society, 2009. **131**(25): p. 8875-8883.
14. Panella, B., et al., *Hydrogen adsorption in metal–organic frameworks: Cu-MOFs and Zn-MOFs compared*. Advanced Functional Materials, 2006. **16**(4): p. 520-524.
15. Rowsell, J.L., et al., *Gas adsorption sites in a large-pore metal-organic framework*. Science, 2005. **309**(5739): p. 1350-1354.
16. Rosi, N.L., et al., *Hydrogen storage in microporous metal-organic frameworks*. Science, 2003. **300**(5622): p. 1127-1129.
17. Zhang, Z., et al., *MOFs for CO₂ capture and separation from flue gas mixtures: the effect of multifunctional sites on their adsorption capacity and selectivity*. Chemical Communications, 2013. **49**(7): p. 653-661.
18. Li, J.-R., R.J. Kuppler, and H.-C. Zhou, *Selective gas adsorption and separation in metal–organic frameworks*. Chemical Society Reviews, 2009. **38**(5): p. 1477-1504.
19. Bae, T.H., et al., *A high-performance gas-separation membrane containing submicrometer-sized metal–organic framework crystals*. Angewandte Chemie, 2010. **122**(51): p. 10059-10062.
20. Lin, R.-B., et al., *Exploration of porous metal–organic frameworks for gas separation and purification*. Coordination Chemistry Reviews, 2019. **378**: p. 87-103.
21. Zhang, H., et al., *Ultrafast selective transport of alkali metal ions in metal organic frameworks with subnanometer pores*. Science advances, 2018. **4**(2): p. eaaq0066.
22. Guo, Y., et al., *Polystyrene sulfonate threaded through a metal–organic framework membrane for fast and selective lithium-ion separation*. Angewandte Chemie, 2016. **128**(48): p. 15344-15348.
23. Li, X., et al., *Fast and selective fluoride ion conduction in sub-1-nanometer metal-organic framework channels*. Nature communications, 2019. **10**(1): p. 1-12.
24. Kadhom, M. and B. Deng, *Metal-organic frameworks (MOFs) in water filtration membranes for desalination and other applications*. Applied Materials Today, 2018. **11**: p. 219-230.
25. Elsayed, E., et al., *CPO-27 (Ni), aluminium fumarate and MIL-101 (Cr) MOF materials for adsorption water desalination*. Desalination, 2017. **406**: p. 25-36.
26. Liu, X., et al., *Highly water-stable zirconium metal–organic framework UiO-66 membranes supported on alumina hollow fibers for desalination*. Journal of the American Chemical Society, 2015. **137**(22): p. 6999-7002.
27. Hu, Z., Y. Chen, and J. Jiang, *Zeolitic imidazolate framework-8 as a reverse osmosis membrane for water desalination: insight from molecular simulation*. The Journal of chemical physics, 2011. **134**(13): p. 134705.
28. Dhakshinamoorthy, A., Z. Li, and H. Garcia, *Catalysis and photocatalysis by metal organic frameworks*. Chemical Society Reviews, 2018. **47**(22): p. 8134-8172.
29. Li, J.-R., J. Sculley, and H.-C. Zhou, *Metal–organic frameworks for separations*. Chemical reviews, 2012. **112**(2): p. 869-932.
30. Rubio-Martinez, M., et al., *New synthetic routes towards MOF production at scale*. Chemical Society Reviews, 2017. **46**(11): p. 3453-3480.

31. Reinsch, H., et al., *A facile "green" route for scalable batch production and continuous synthesis of zirconium MOFs*. European Journal of Inorganic Chemistry, 2016. **2016**(27): p. 4490-4498.
32. Czaja, A.U., N. Trukhan, and U. Müller, *Industrial applications of metal-organic frameworks*. Chemical Society Reviews, 2009. **38**(5): p. 1284-1293.
33. Huelsenbeck, L., et al., *A Generalized Approach for Rapid Aqueous MOF Synthesis by Controlling Solution pH*. Crystal Growth & Design, 2020.
34. Gnansounou, E. and A. Dauriat, *Technoeconomic analysis of lignocellulosic ethanol*, in *Biofuels*. 2011, Elsevier. p. 123-148.
35. Wright, M.M., et al., *Techno-economic analysis of biomass fast pyrolysis to transportation fuels*. Fuel, 2010. **89**: p. S2-S10.
36. Polyzoidis, A., et al., *Continuous microreactor synthesis of ZIF-8 with high space-time-yield and tunable particle size*. Chemical Engineering Journal, 2016. **283**: p. 971-977.
37. Li, F., et al., *Hierarchically porous metal-organic frameworks: green synthesis and high space-time yield*. Industrial & Engineering Chemistry Research, 2018. **57**(28): p. 9136-9143.
38. Ayres, R.U., *Life cycle analysis: A critique*. Resources, conservation and recycling, 1995. **14**(3-4): p. 199-223.
39. Ciambrone, D.F., *Environmental life cycle analysis*. 1997: CRC Press.
40. Clarens, A.F., et al., *Environmental life cycle comparison of algae to other bioenergy feedstocks*. Environmental science & technology, 2010. **44**(5): p. 1813-1819.
41. Abid, H.R., et al., *Nanosize Zr-metal organic framework (UiO-66) for hydrogen and carbon dioxide storage*. Chemical Engineering Journal, 2012. **187**: p. 415-420.
42. Huang, Q., et al., *Experimental and computational investigation of CO₂ capture on mix-ligand metal-organic framework UiO-66*. Energy Procedia, 2017. **105**: p. 4395-4401.
43. Huang, A., L. Wan, and J. Caro, *Microwave-assisted synthesis of well-shaped UiO-66-NH₂ with high CO₂ adsorption capacity*. Materials Research Bulletin, 2018. **98**: p. 308-313.
44. Jiang, Y., et al., *A new UiO-66-NH₂ based mixed-matrix membranes with high CO₂/CH₄ separation performance*. Microporous and Mesoporous Materials, 2019. **274**: p. 203-211.
45. Li, Z., et al., *Deep eutectic solvents appended to UiO-66 type metal organic frameworks: Preserved open metal sites and extra adsorption sites for CO₂ capture*. Applied Surface Science, 2019. **480**: p. 770-778.
46. DeSantis, D., et al., *Techno-economic analysis of metal-organic frameworks for hydrogen and natural gas storage*. Energy & Fuels, 2017. **31**(2): p. 2024-2032.
47. *Average Price of Electricity to Ultimate Customers by End-Use Sector*. Available from: https://www.eia.gov/electricity/monthly/epm_table_grapher.php?t=epmt_5_6_a.
48. Pakamorè, I., et al., *An ambient-temperature aqueous synthesis of zirconium-based metal-organic frameworks*. Green Chemistry, 2018. **20**(23): p. 5292-5298.
49. Pan, Y., et al., *Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) nanocrystals in an aqueous system*. Chemical Communications, 2011. **47**(7): p. 2071-2073.
50. Bao, Q., et al., *Rapid synthesis of zeolitic imidazolate framework-8 (ZIF-8) in aqueous solution via microwave irradiation*. Inorganic Chemistry Communications, 2013. **37**: p. 170-173.
51. Avci-Camur, C., et al., *Aqueous production of spherical Zr-MOF beads via continuous-flow spray-drying*. Green chemistry, 2018. **20**(4): p. 873-878.
52. Cadot, S., et al., *A water-based and high space-time yield synthetic route to MOF Ni₂(dhtp) and its linker 2, 5-dihydroxyterephthalic acid*. Journal of Materials Chemistry A, 2014. **2**(42): p. 17757-17763.
53. Grande, C.A., et al., *Life-cycle assessment as a tool for eco-design of metal-organic frameworks (MOFs)*. Sustainable Materials and Technologies, 2017. **14**: p. 11-18.

54. Liu, L., et al., *Metal–Organic Gel Material Based on UiO-66-NH₂ Nanoparticles for Improved Adsorption and Conversion of Carbon Dioxide*. Chemistry–An Asian Journal, 2016. **11**(16): p. 2278-2283.
55. Cao, Y., et al., *UiO-66-NH₂/GO composite: synthesis, characterization and CO₂ adsorption performance*. Materials, 2018. **11**(4): p. 589.
56. Molavi, H., et al., *Enhancing CO₂/N₂ adsorption selectivity via post-synthetic modification of NH₂-UiO-66 (Zr)*. Microporous and Mesoporous Materials, 2018. **257**: p. 193-201.
57. Towler, G. and R. Sinnott, *Chemical engineering design: principles, practice and economics of plant and process design*. 2012: Elsevier.
58. Sinnott, R., *Chemical engineering design*. Vol. 6. 2014: Elsevier.
59. Wernet, G., et al., *The ecoinvent database version 3 (part I): overview and methodology*. The International Journal of Life Cycle Assessment, 2016. **21**(9): p. 1218-1230.
60. Aguilera-Sigalat, J. and D. Bradshaw, *A colloidal water-stable MOF as a broad-range fluorescent pH sensor via post-synthetic modification*. Chemical Communications, 2014. **50**(36): p. 4711-4713.
61. Yin, B., et al., *Zirconium tetrachloride and zirconia preparation process by secondary chlorination*. 2018, Xinjiang Jingshuo New Materials Co., Ltd., Peop. Rep. China . p. 10pp.
62. Sun, Y., et al., *Crystallization process and device for preparation of zirconyl chloride*. 2003, Guangdong Orient Zirconic Ind Sci and Tech Co., Ltd., Peop. Rep. China . p. 9 pp.
63. Guo, Z., et al., *Method for production of high-purity zirconium oxychloride and coproduction of silicon tetrachloride by zircon sand fluidizing chlorination*. 2015, Peop. Rep. China . p. 16pp.
64. Chen, J., et al., *Production method of zirconium oxychloride using membrane treatment technology*. 2018, Longmang Billions Group Co., Ltd., Peop. Rep. China . p. 4pp.
65. Li, M., et al., *Method for preparing diazonium salt by depolymerizing waste polyester fibers using ethylene glycol*. 2014, Jiangnan University, Peop. Rep. China . p. 9pp.
66. Skibo, E.B. and J.H. Gilchrist, *Synthesis and electrochemistry of pyrimidoquinazoline-5, 10-diones. Design of hydrolytically stable high potential quinones and new reductive alkylation systems*. The Journal of Organic Chemistry, 1988. **53**(18): p. 4209-4218.
67. Guinée, J.B. and E. Lindeliger, *Handbook on life cycle assessment: operational guide to the ISO standards*. Vol. 7. 2002: Springer Science & Business Media.
68. Wu, F., Z. Zhou, and A.L. Hicks, *Life cycle impact of titanium dioxide nanoparticle synthesis through physical, chemical, and biological routes*. Environmental science & technology, 2019. **53**(8): p. 4078-4087.
69. Lokesh, K., et al., *Hybridised sustainability metrics for use in life cycle assessment of bio-based products: resource efficiency and circularity*. Green Chemistry, 2020. **22**(3): p. 803-813.
70. Goedkoop, M., et al., *ReCiPe 2008*. 2009. **1**: p. 1-126.
71. White, R., et al., *Techno-Economic and Life Cycle Impacts Analysis of Direct Methanation of Glycerol to Bio-Synthetic Natural Gas at a Biodiesel Refinery*. Energies, 2019. **12**(4): p. 678.
72. Caramazana-Gonzalez, P., et al., *Assessing the life cycle environmental impacts of titania nanoparticle production by continuous flow solvo/hydrothermal syntheses*. Green Chemistry, 2017. **19**(6): p. 1536-1547.
73. Küsgens, P., et al., *Characterization of metal-organic frameworks by water adsorption*. Microporous and Mesoporous Materials, 2009. **120**(3): p. 325-330.
74. Biswas, S. and P. Van Der Voort, *A general strategy for the synthesis of functionalised UiO-66 frameworks: characterisation, stability and CO₂ adsorption properties*. European Journal of Inorganic Chemistry, 2013. **2013**(12): p. 2154-2160.
75. Cao, Y., et al., *Preparation and enhanced CO₂ adsorption capacity of UiO-66/graphene oxide composites*. Journal of Industrial and Engineering Chemistry, 2015. **27**: p. 102-107.

76. MacDowell, N., et al., *An overview of CO₂ capture technologies*. Energy & Environmental Science, 2010. **3**(11): p. 1645-1669.
77. Cheng, F., H. Luo, and L.M. Colosi, *Slow pyrolysis as a platform for negative emissions technology: An integration of machine learning models, life cycle assessment, and economic analysis*. Energy Conversion and Management, 2020. **223**: p. 113258.
78. Cheng, F., M.D. Porter, and L.M. Colosi, *Is hydrothermal treatment coupled with carbon capture and storage an energy-producing negative emissions technology?* Energy Conversion and Management, 2020. **203**: p. 112252.
79. Idem, R., et al., *Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the boundary dam CO₂ capture demonstration plant*. Industrial & engineering chemistry research, 2006. **45**(8): p. 2414-2420.
80. Singh, D., et al., *Techno-economic study of CO₂ capture from an existing coal-fired power plant: MEA scrubbing vs. O₂/CO₂ recycle combustion*. Energy conversion and Management, 2003. **44**(19): p. 3073-3091.
81. Alie, C., et al., *Simulation of CO₂ capture using MEA scrubbing: a flowsheet decomposition method*. Energy conversion and management, 2005. **46**(3): p. 475-487.
82. Yeh, A.C. and H. Bai, *Comparison of ammonia and monoethanolamine solvents to reduce CO₂ greenhouse gas emissions*. Science of the Total Environment, 1999. **228**(2-3): p. 121-133.
83. Zhu, D., et al., *Selection of blended solvents for CO₂ absorption from coal-fired flue gas. Part 1: Monoethanolamine (MEA)-based solvents*. Energy & fuels, 2012. **26**(1): p. 147-153.
84. Gao, J., et al., *Integration study of a hybrid solvent MEA-Methanol for post combustion carbon dioxide capture in packed bed absorption and regeneration columns*. Separation and Purification Technology, 2016. **167**: p. 17-23.
85. Li, K., et al., *Systematic study of aqueous monoethanolamine-based CO₂ capture process: model development and process improvement*. Energy Science & Engineering, 2016. **4**(1): p. 23-39.
86. Trickett, C.A., et al., *The chemistry of metal-organic frameworks for CO₂ capture, regeneration and conversion*. Nature Reviews Materials, 2017. **2**(8): p. 1-16.