Life-cycle assessment as a tool for eco-design of metal-organic frameworks (MOFs)

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A B S T R A C T

Metal-organic framework (MOF) materials are porous materials with high surface area that offer enormous flexibility of design and tailoring of its surface properties to be used in diverse chemical processes. Most of the reported properties of MOF materials were evaluated in powder materials produced in small scale where the synthesis has been optimized to obtain crystalline powders. Ideally, the industrialization of these materials will also be associated to efficient scalable synthesis protocols. Moreover, for these materials to be used as environmental-benign materials, their synthesis has to be sustainable.

We present a cradle-to-gate life-cycle assessment of four different synthesis protocols to produce a MOF material (CPO-27-Ni also termed as MOF-74 and DOBDC) which is one suitable novel adsorbent material for carbon capture and storage (CCS) technologies. We have demonstrated that using a LCA is possible to idealize a methodology for eco-design of MOF materials. With our analysis we have determined that the impact of using solvents in the synthesis is considerable. Moreover, surprisingly, the LCA analysis helped us identifying that the utilization of solvents for the cleaning and purification steps has an equally (or even larger) impact in the environmental indicators. Utilization of solvents should be avoided if possible or reutilization strategies should be envisaged if is not possible to eliminate them.

1. Introduction

The synthesis of a myriad of new porous materials has increased the prospects of using advanced separation technologies in applications where targeted properties are required. Several actual societal challenges where novel and sustainable technologies are required are: carbon dioxide capture and storage (CCS), development of bio-based economy, increase of utilization of renewable energy sources and increased efficiency of energy utilization. All these different markets will benefit from tailored properties that novel materials can provide.

A novel material for environmentally driven applications should not only show high efficiency, but should also show a low-emission and sustainable synthesis. For example, if a material used for CCS produces hundreds of kilos of CO_2 to fabricate 1 kg of material, it should be used many times to sequester such amount of CO_2 only to become carbon neutral. For the time required to reach carbon neutrality, such CCS process will not be beneficial to the environment. For this reason, is crucial to focus on efficient but also sustainable materials.

A key step to quantify the environmental impact of materials is thus required. Life Cycle Assessment (LCA) is a standardized methodology to assess the environmental impact of a product. It takes into account its whole life cycle, starting from the extraction of metals, minerals, power, etc. (cradle) necessary to produce the chemicals for its manufacture, including its utilization and also accounting for its disposal (grave). LCA has proved to be a useful tool for environmental impacts assessment in the energy and fuels sector [1–7]. So far, LCA conducted to support decision for policy development, have been based on ISO standards (ISO 14040 and 14044).

Metal-organic frameworks are a special class of porous materials [8–10]. The flexibility of design of MOF materials combining different metals with several possible organic linkers makes the number of possible MOFs almost unlimited. The linkage generates a one, two or three-dimensional framework whose skeleton contains both organic and inorganic units. These structures offer a wide range of tunable properties that depend both from the inorganic joints and from the organic linkers. Since organic linkers (typically organic acids) are used, it is common practice to use organic solvents in the synthesis of MOF materials. The nature of the solvents is normally defined by the solubility of the organic linker in them aiming to obtain high yields.

Several studies considered MOF materials for CO_2 capture [11–13].

One material with interesting properties for CO_2 capture is termed CPO-27 [14]. This material has been reported from two groups almost at the same time (SINTEF in Europe and Yaghi's group in USA) and is known either by the name of CPO-27 or MOF-74 or DOBDC [15]. This material can be produced with different metals as cations rendering different properties. In this work, nickel was used as cation and we have thus denoted the material as CPO-27-Ni. The reason for using nickel is that this material has shown a very good selectivity towards CO_2 from flue gases and is stable over time. The sustainability of using a new material like CPO-27-Ni depends on an efficient separation process for maximizing its utilization (process engineering) and its manufacture (material science). Once that utilization of MOFs is not commercial for CCS, the energy related to its utilization and also the life of the CPO-27-Ni adsorbent are not yet known. For this reason, only a cradle-to-gate approach is presented. The "gate" is defined as produced powder of MOF material.

In this work, we present a LCA of four different synthesis routes to produce CPO-27-Ni taking 1 kg of produced powder of CPO-27-Ni as the functional unit. From the several impact indicators calculated in this study, we have used the climate-change impact indicator as the most important one since the utilization of solvents is only at research stage. Other indicators of ecotoxicity can be showstoppers at a later stage of the process development. The objective is to present the impact of synthesis and cleaning procedures aiming to obtain an improved fabrication route, or eco-design, in terms of material environmental sustainability. Additionally, a novel synthesis route using only water as reacting medium and cleaning agent is described.

2. MOF synthesis and characterization

In order to perform a structured LCA, the MOF synthesis was divided into a series of sequential unitary processes that require chemicals (reactants, solvents and cleaning agents) and/or power (heat and/or electricity) to operate. The generic synthesis procedure is depicted in Fig. 1 and can be used for synthesis of many porous materials other than MOFs. The LCA boundaries depicted in this Figure indicates that all items located inside the boundaries were accounted for in the LCA, including the production of the starting chemicals and the energy used for each of these unitary processes was taken into account.

Four different samples of CPO-27-Ni were prepared using different synthesis routes with different solvent compositions and cleaning procedures. The main difference between these recipes is the chemicals used in synthesis and cleaning steps. The last route tested (IV) presents a slightly higher conversion, result of a different synthesis technology.

2.1. Synthesis route I

This procedure is based on the procedure described by Kizzie et al. [16]: 0.239 g (1.2 mmol) 2,5-dihydroxyterephtalic acid (> 98% from Carbosynth UK) and 1,19 g (4.09 mmol) Ni(II)-nitrate 6H_2O (from Sigma-Aldrich) were dissolved in a solvent mixture consisting of 33.3 mL DMF, 33.3 mL EtOH and 33.3 mL H_2O. After vigorous mixing, the solvent was transferred to a 200 mL Teflon liner at ambient temperature. The liner was introduced to a 200 mL autoclave, which was sealed and heated to 100°C for 24 h. The autoclave was cooled and the content was centrifuged. The product powder was washed three times with 100 mL portions of MeOH. Yield 0.280 g of Ni($C_8O_6H_2$)$_{0.5}$, 75% yield based on the limiting component, the linker.

2.2. Synthesis route II

This procedure is based on the procedure described by Dietzel et al. [14]. A solution of 0.713 g 2,5-dihydroxyterephtalic acid (> 98% from Carbosynth UK) in 12 mL THF and a solution of 1.792 Ni-acetate 4 H_2O (99% from Aldrich) in 12 mL water were mixed in a Teflon liner at ambient temperature yielding a clear green solution. The liner was introduced to a 50 mL autoclave, which was sealed and heated to 110 °C for 70 h. The autoclave was cooled for 2 h before it was opened. The formed slurry was centrifuged and the dirt-yellow product powder was washed three times with 30 mL portions of water with centrifugation between each washing step. The final powder was dried under vacuum at ambient temperature. Yield is 0.714 g Ni($C_8O_6H_2$)$_{0.5}$, corresponding to 64%.

2.3. Synthesis route III

This is a modified version of route II using only water during the synthesis but a THF step for washing. A suspension of 0.713 g 2,5-dihydroxyterephtalic acid (> 98% from Carbosynth UK) in 12 mL water and a solution of 1.792 Ni-acetate 4 H_2O (99% from Aldrich) in 12 mL water were mixed in a Teflon liner at ambient temperature yielding a clear green solution. The liner was introduced to a 50 mL autoclave, which was sealed and heated to 110 °C for 70 h. The autoclave was cooled for 2 h before it was opened. The formed slurry was centrifuged and the dirt-yellow product powder was washed three times with centrifugation between each washing step: first with 30 mL water, then with 30 mL THF and a final wash with 30 mL water. The final powder was dried under vacuum at ambient temperature. Yield is 0.714 g Ni($C_8O_6H_2$)$_{0.5}$, corresponding to 64%.
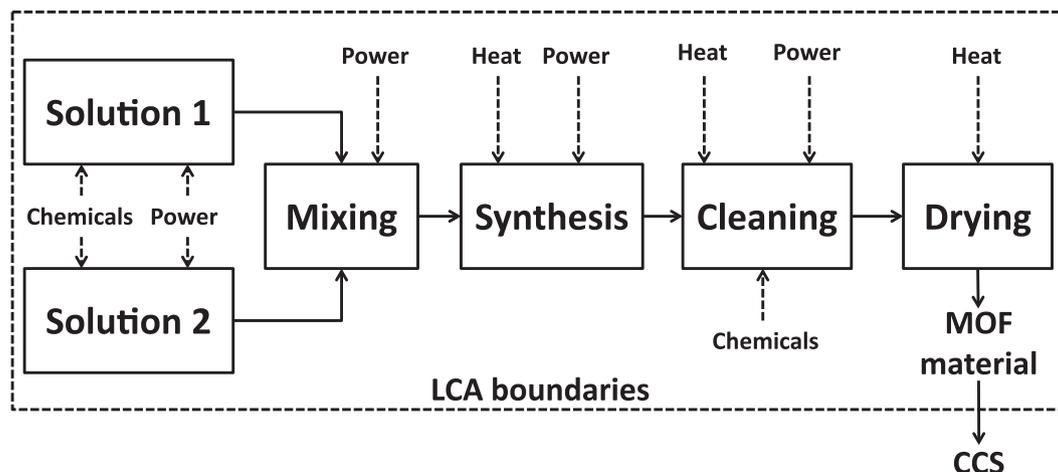

Fig. 1. LCA boundaries used in this work for the synthesis of CPO-27-Ni metal-organic framework with identification of inputs and outputs of chemicals and energy for different synthesis steps.

Table 1
Amount of chemicals to be used to synthesize 1 kg of CPO-27-Ni using different preparation recipes.

Synthesis route	Type Ni-precursor	Mass Ni source [kg]	Mass [kg] linker	Solvent for synthesis [L]	Yield[a] [%]	Solvent for cleaning [L]	BET surface area [m^2/g]
I [16]	Ni(II)-nitrate 6 H$_2$O	4.25	0.854	119 L DMF 119 L EtOH 119 L H$_2$O	75	1071 L MeOH	992
II [14]	Ni(II)-acetate 4 H$_2$O	2.51	0.999	16.8 L THF 16.8 L H$_2$O	64	126 L H$_2$O	1269
III	Ni(II)-acetate 4 H$_2$O	2.51	0.999	33.6 L H$_2$O	64	42 L THF 84 L H$_2$O	1150
IV	Ni(II)-acetate 4 H$_2$O	2.59	1.029	33.6 L H$_2$O	61	130 L H$_2$O	1297

[a] Yield is calculated based on linker but routes 2–4 have a stoichiometric ratio.

Table 2
Details of methods used for calculations of the different impact indicators.

| Impact category	Indicator	Unit	Method
Climate change	Bern model – Global Warming Potential (GWP)	kg CO$_2$ equivalent	[22]
Ozone depletion		kg CFC-11 equivalent	
Particulate matter	Intake fraction for fine particles	kg PM$_{2.5}$ equivalent	RiskPoll model [18,19]
Ionizing radiation HH		kBq U235 equivalent	
Ionizing radiation E (interim)		CTUe	
Photochemical ozone formation		kg NMVOC equivalent	
Acidification		molc H + equivalent	
Terrestrial eutrophication		molc N equivalent	
Freshwater eutrophication	Fraction of nutrients reaching freshwater end compartment	kg P equivalent	EUTREND model [20] as implemented in ReCiPe
Marine eutrophication		kg N equivalent	
Freshwater ecotoxity	Comparative Toxic Unit for Ecosystems (CTUe)	CTUe	USEtox
Land use		kg C deficit	
Water resource depletion		m^3 water equivalent	
Resource depletion, mineral, fossil and renewable	Scarcity	kg Sb equivalent	CML 2002 [21]
Human health (cancer and non-cancer effects)		CTUh	
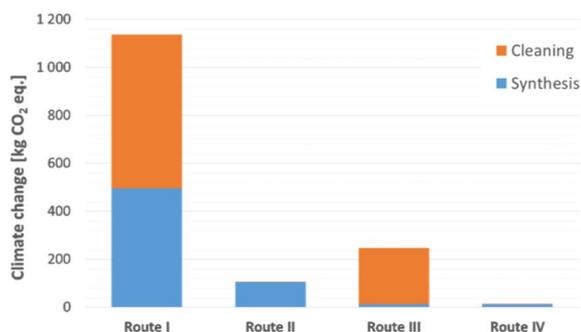
Fig. 2. Climate change indicator for production of CPO-27-Ni: total emissions of kg CO$_2$ eq. to produce 1 kg of MOF.

2.4. Synthesis route IV

This is a novel route using only water as solvent for all steps. A suspension of 0.713 g (3.6 mmol) 2,5-dihydroxyterephtalic acid (> 98% from Carbosynth UK) in 12 mL water and a solution of 1.792 g (7.2 mmol) Ni(II)-acetate 4 H$_2$O (99% from Aldrich) in 12 mL water were mixed in a Teflon liner at ambient temperature yielding a clear green solution. The liner was introduced to a 50 mL autoclave that was sealed and heated to 110 °C for 70 h. The autoclave was cooled for 2 h before it was opened. The formed slurry was centrifuged and the dirt-yellow product powder was washed three times with 30 mL portions of water. The final powder was dried under vacuum at ambient temperature, then at 130 °C overnight. Dry yield is 0.693 g Ni(C$_8$O$_6$H$_2$)$_{0.5}$, which corresponds to 62%.
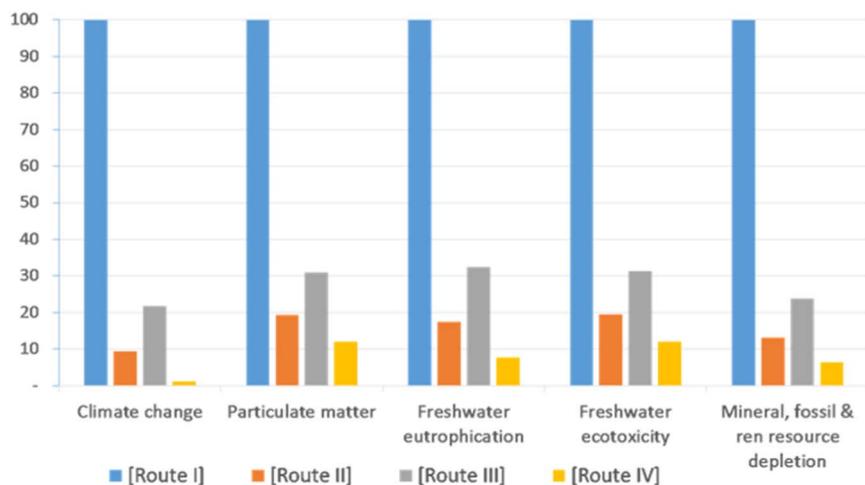
Fig. 3. LCA analysis on five different impact indicators for production of 1 kg of CPO-27-Ni.

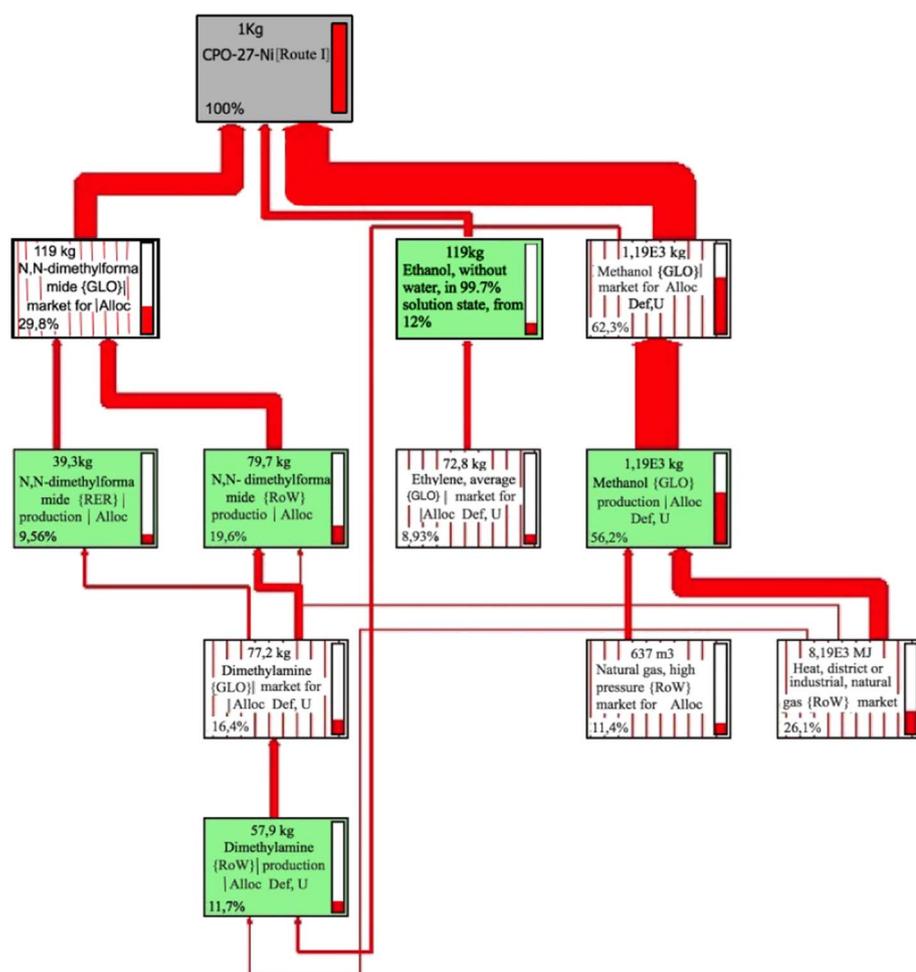Based on the chemicals used for lab-scale synthesis, a weight normalization of the synthesis amounts was done. The idea was to account for the necessary chemicals required to produce 1 kg of MOF powder that will be used as functional unit for the LCA. The quantities for such production are shown in Table 1.

3. Description of life cycle assessment

In order to normalize the LCA to a standard basis, the analysis considered 1 kg of powder of CPO-27-Ni as the functional unit. In order to quantify the amount of chemicals and energy spent in the production, it was assumed that the same CPO-27-Ni properties will be maintained in the industrial scale-up of this material. Moreover, the duration of the synthesis steps (that was given in all synthesis protocols) was assumed to remain the same in a scaled up process in order to account for power consumption. The amount of chemicals used in each route is presented in Table 1.

The ILCD 2011 Midpoint method v1.03 has been chosen for this study. This method was released by the European Commission, Joint Research Centre in 2012. It supports the correct use of the characterization factors for impact assessment as recommended in the ILCD guidance document [17]. The analysis considers the production of 1 kg of CPO-27-Ni and it does not account for its CCS utilization and disposal, so the LCA is not cradle-to-grave. Due to lack of data on utilization of this material, its energetic performance in industrial scale, the period of its service life and the disposal routines, it is not possible to perform a cradle-to-grave analysis. In this sense, a cradle-to-gate analysis is presented.

The analysis has been performed with the software Simapro v8.0.4.

and we have selected 5 of the 16 midpoint impact categories in order to have a better understanding of the results. These indicators are: climate change, particulate matter, freshwater euthrophication, freshwater ecotoxicity and resource depletion (mineral, fossil and renewable). From these indicators, more emphasis will be given to the climate change indicator, which relates the amount of CO$_2$ generated to produce the CPO-27-Ni from components present in nature and energy (either heat or electricity). The inventory database Ecoinvent v3 was used. An attributional analysis was performed since the major aim of the study is to generate knowledge without implying a decision context that would account for potential additional consequences in other systems. Details on the calculations of the different indicators are given in Table 2.

4. Results and discussion

4.1. MOF production

The four different routes have successfully produced CPO-27-Ni material with the same CO2 adsorption capabilities. The same structure was characterized by X-Ray diffraction. However, the surface area obtained in the first recipe is not very high, as reported in Table 1. The surface area increase is probably the result of less organic molecules that were still somehow retained in the pores of the MOF material. However, in the screening of CO$_2$ isotherms made on all the produced materials, relatively small differences were observed between the samples and thus we assume that all of them have comparable properties for utilization in CCS.

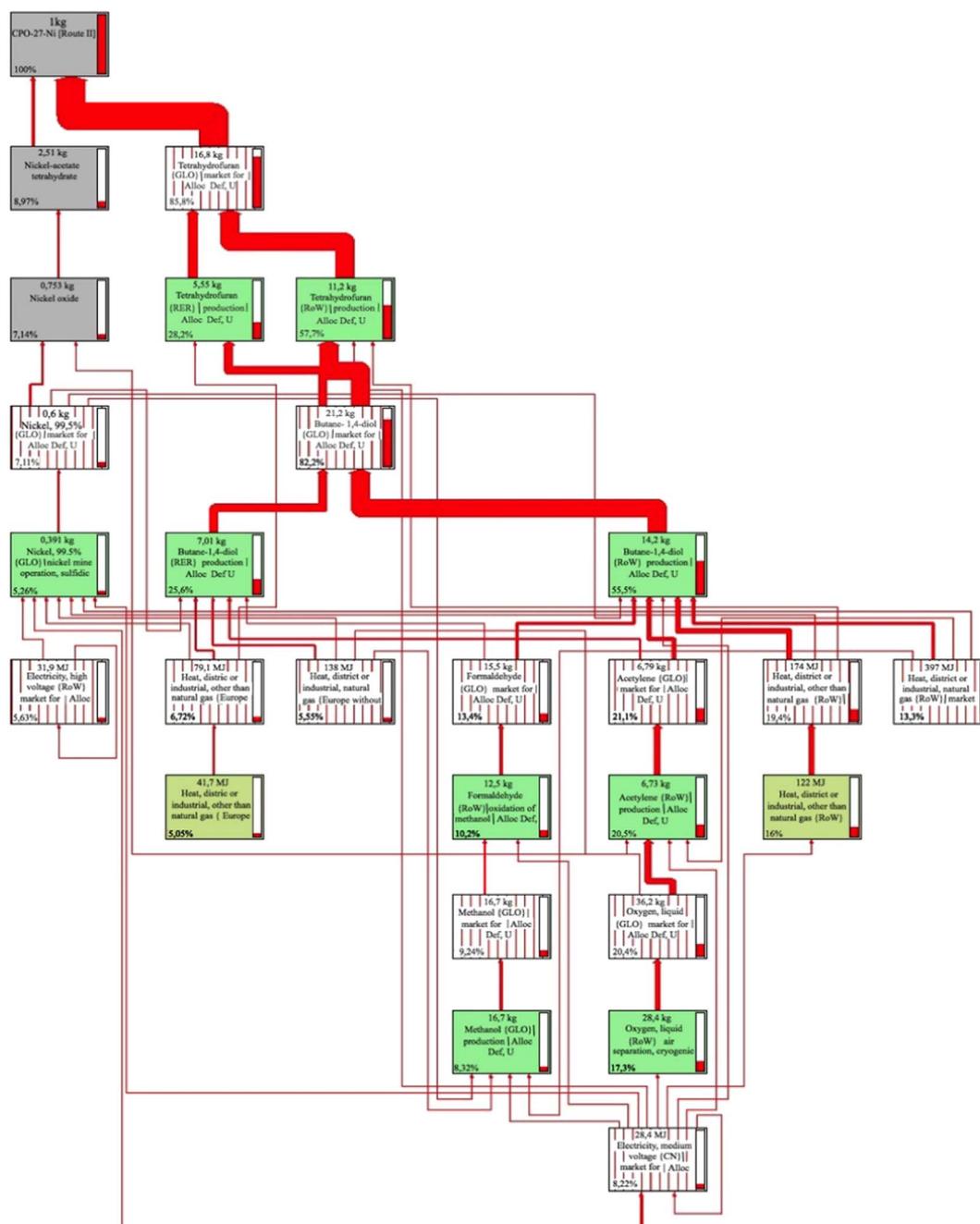As can be noted, the first recipe utilizes a large amount of solvents

Fig. 5. LCA process tree from the LCA modelling of Route II.

and then the amount of chemicals is sequentially decreased in successive recipes. Additionally, a large amount of solvent is used for cleaning the remaining of solvent and unreacted linker material. The recovery of solids in the first route is higher than in the others because the dilution of the synthesis tends to produce larger crystals and filtration losses are smaller. Moreover, it is known that some crystal losses occur in smaller scale synthesis. It is thus expected that the industrial application will render better yield results and thus this analysis is slightly conservative.

4.2. LCA results

According to what is presented in Fig. 1, chemicals and energy (heat and electricity) are needed in different unitary processes to produce the MOF material.

A summary of the results obtained in terms of CO_2 eq. emissions is shown in Fig. 2. This figure clearly shows that the environmental

impact of the CPO-27 is dominated by the utilization of solvents, either in the synthesis or in the cleaning steps. By completely eliminating the utilization of solvents and making the MOF synthesis completely water-based, it was possible to reduce almost 100 times the environmental impact of the synthesis (from 1136.2 to 12.3 kg CO_2 eq.). The remaining emissions when no solvents are used correspond to the production of the necessary chemicals and to the energy used in the synthesis.

Significant reduction on the other impact indicators has also been achieved by making the synthesis solvent-free and by not using solvents in the cleaning step either. Their reduction is shown in Fig. 3, as percentage reduction taking Route I as reference. For all impact categories, results are similar: Route IV which uses only water has less impact than others. As shown in Fig. 3, it exists a correlation between the amount of solvent used and the value of the environmental impact indicators.

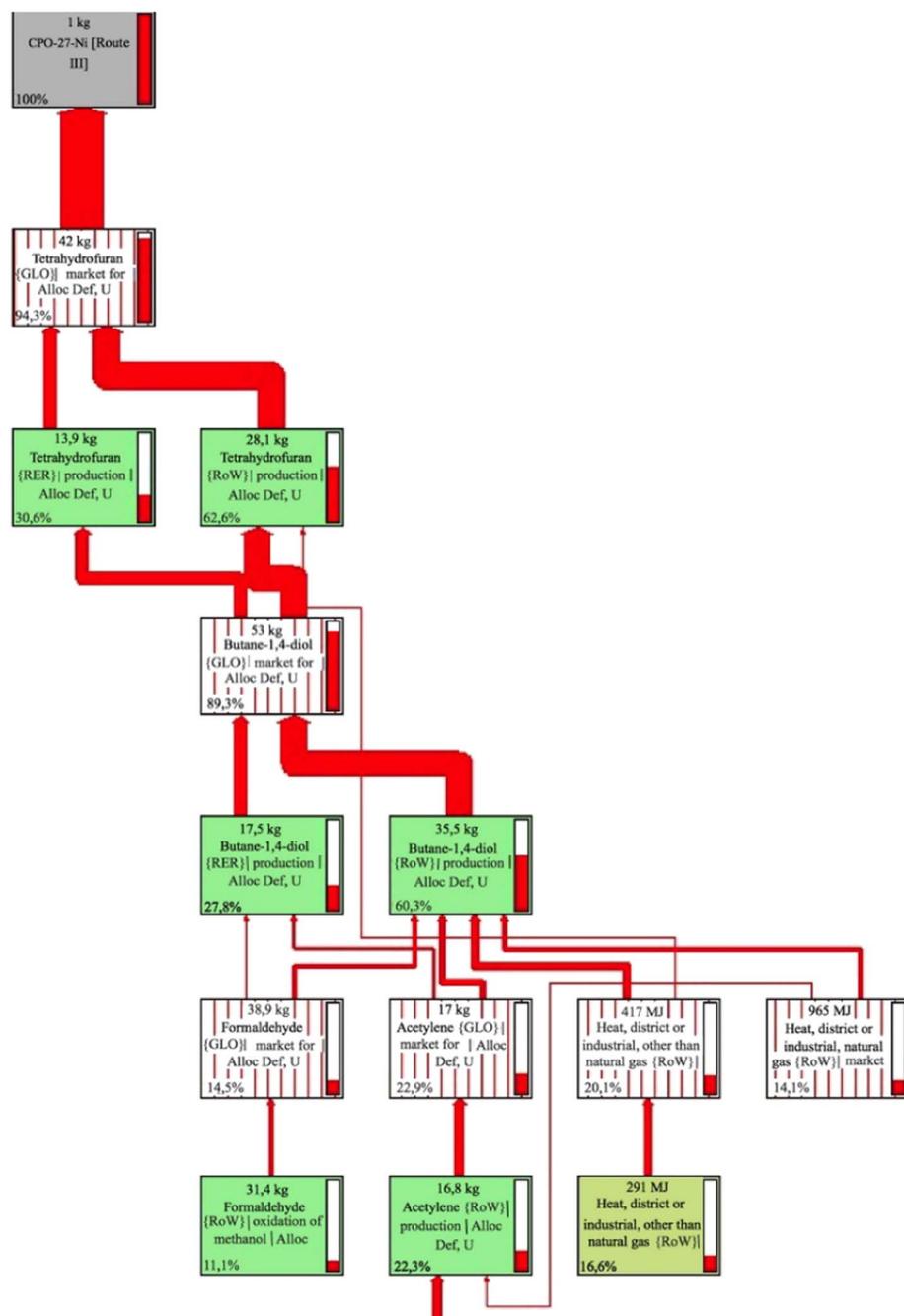The effect of the different solvents can also be noted in the

freshwater toxicity where the impact of ethanol and methanol is much smaller than the one given by DMF and particularly THF. The differences in the resources depletion due to the utilization of solvents is also clear, although in this case removing all solvents from the system results in a change of impact indicator of one order of magnitude.

The details of the LCA methodology used to obtain the results presented, are shown in Figs. 4–7 for the different synthesis routes.

4.3. Sustainability

The development of new materials can have a substantial contribution in mitigation of greenhouse gases, as long as their production is done in a sustainable manner.

Improving the synthesis of new materials imply that each of the steps shown in Fig. 1 has been optimized. What our results demonstrated is that avoiding the utilization of solvents is a key step to achieve low climate change impact. In practical terms avoiding solvents also means that operation safety rules will be less tight, providing more operational flexibility and reduce the capital cost of the manufacture.

However, solvents cannot be avoided in the synthesis of some materials. For such cases, this approach will indicate that for a large-scale production of such a material, there is a need to recycle the solvent or to look for another solvent as alternative to reduce its environmental footprint. Having such results and the economic costs of manufacturing, it should be possible to trade-off performance and greenhouse gas emissions so that the economic profitability meets sustainability. Thus, this is another example of win-win situation where benefits to the environment result in straightforward and measurable economic benefits in production.

Fig. 7. LCA process tree from the LCA modelling of Route IV.
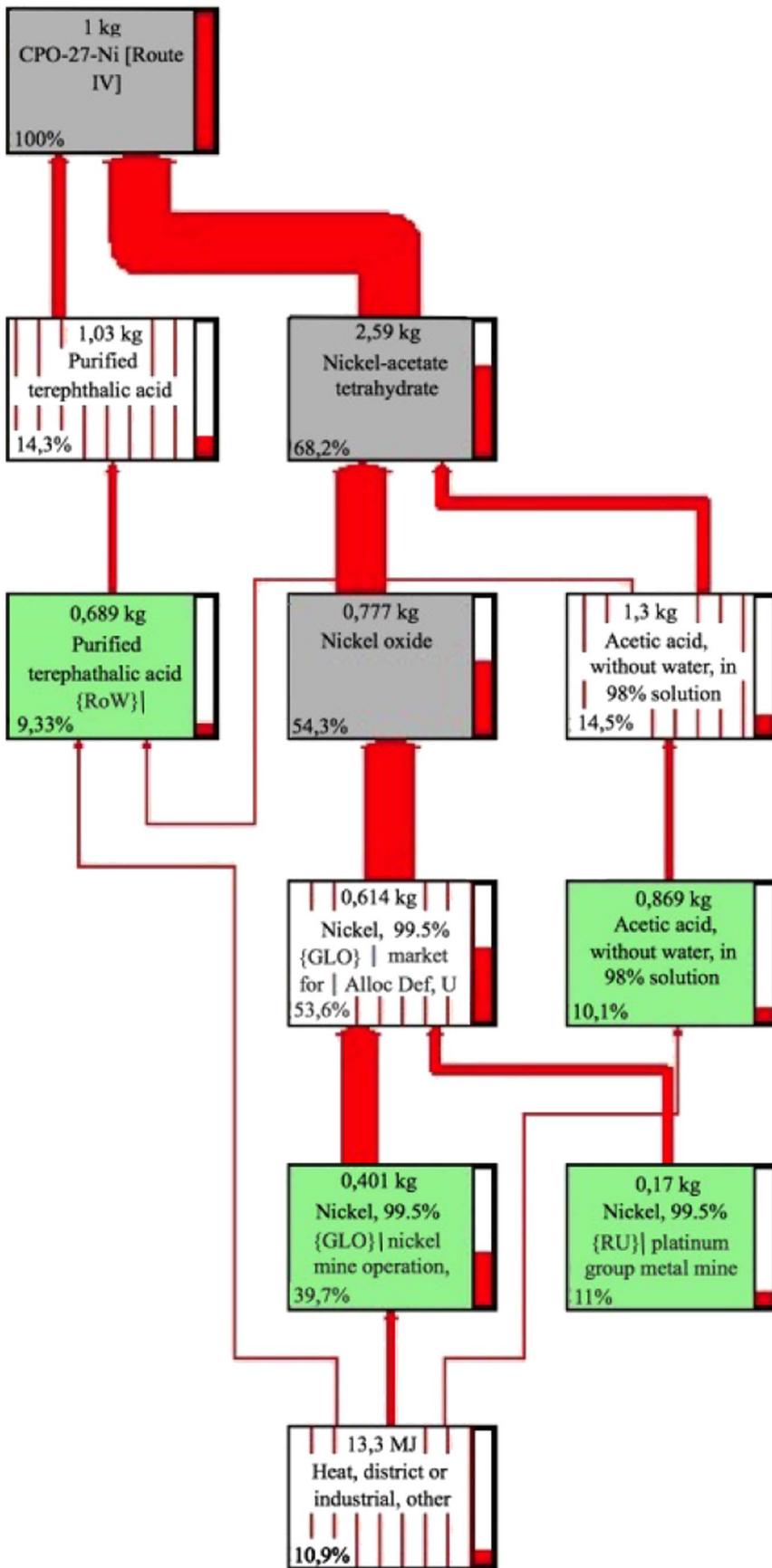
5. Conclusions

CPO-27-Ni metal-organic framework (MOF) was synthesized using four different recipes, including a novel recipe based only on utilization of water as solvent. We have used a cradle-to-gate life-cycle assessment (LCA) to demonstrate the impact of utilization of solvents in the environmental footprint of MOF production. From the different impact indicators, we have observed that by removing the organic solvents from the synthesis it is possible to reduce in about two orders of magnitude the emissions of CO_2 in the production of the MOF material and also a reduction of one order of magnitude in the freshwater toxicity and resource depletion.

We believe that this type of study can serve as an initial screen tool to assess the environmental performance of novel materials. Moreover, it can be used for establishing the necessity of recycling a given solvent or to find an alternative solvent that significantly reduces the environmental impact of novel materials.

Acknowledgments

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