Assessing the environmental impact and payback of carbon nanotube supported CO₂ capture technologies using LCA methodology

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Abstract

Climate change caused by excessive CO_2 emissions in the atmosphere has attracted widespread public concern in recent years. Current industrial methods generally utilize monoethanolamine for CO_2 capture; however, the CO_2 regeneration requires a high temperature and energy demand during every adsorption/desorption process, along with material losses. Many solid amines with high capture capacity and stability are developed as adsorbents to overcome the limitations. However, the environmental impacts caused by adsorbents themselves are not holistically considered and discussed; meanwhile, material syntheses and consumptions are also associated with CO_2 emission. To determine the environmental impacts and identify hotspots of novel CO_2 capture adsorbents, two carbon nanotube supported polyethyleneimine, physically adsorbed and covalently bonded, were compared with traditional monoethanolamine method using life cycle assessment. The carbon payback periods were also analyzed to gain understanding on whether the currently evaluated novel materials are suitable for industrial application. Results suggest that, material usage, especially carbon nanotubes, contributes the majority of the overall environmental impacts for both types of carbon nanotube supported polyethyleneimine. Meanwhile, their carbon payback periods are over 40 times longer than monoethanolamine during the synthesis phase. However, the energy consumption of physically adsorbed polyethyleneimine saves up to 60% compared to monoethanolamine in every adsorption/desorption cycle due to its lower heat capacity. In addition, the rate of cumulative CO_2 remission for carbon nanotube supported polyethyleneimine is twice higher than monoethanolamine, indicating the potential application for industrial CO_2 capture. Overall, our study indicates that current status of solid amine has a potential in CO_2 capture, but requires much improvements. Future research should pay attention on decreasing the initial material synthesis and increasing the product life time due to their high environmental tradeoffs. Meanwhile, our study highlights that

38 unilateral emphasis of the CO_2 capture efficiency by novel materials may not be adequate,
39 comprehensive considerations should be focused on the comparison throughout material life
40 cycles including use and preparation phases.

41

42

43 Keywords: CO_2 capture; carbon nanotube; solid amine; payback period; life cycle assessment.

Abbreviations

GHG: greenhouse gas; MEA: monoethanolamine; PEI: polyethyleneimine; DMF: dimethylformamide; CNT: carbon nanotubes; CNT-PEI: CNT supported PEI; Phy-CNT-PEI: physiosorbed CNT supported PEI; Cov-CNT-PEI: covalently bound CNT supported PEI; LCA: life cycle assessment; OD: ozone depletion; GW: global warming; PS: photochemical smog; AC: acidification; EU: eutrophication; HHC: human health carcinogenic; HHNC: Human health noncarcinogenic; RE: respiratory effects; EC: ecotoxicity; FF: fossil fuel depletion; USLCI: U.S. Life Cycle Inventory; TRACI: tool for the reduction and assessment of chemical and other environmental impacts; A/D: adsorption/desorption.

1. Introduction

The use of fossil fuels, changes in land, industries, transportation and buildings have given rise to an increase in greenhouse gas (GHG) emissions (US EPA, 2015). The increased level of GHG emission leads to climate change and global warming, which are unequivocal facts and cause growing concern. Carbon dioxide (CO_2) is the biggest contributor to global GHG with an approximately 80% share (Pachauri and Meyer, 2014). In addition, the result of the latest measurement for CO_2 level (in March 2020) reported by the National Aeronautics and Space Administration (NASA) is 413.03 parts per million in Mauna Loa Observatory, Hawaii, which is the highest level recorded in the past 650,000 years. These realizations pave new ways to develop sustainable solutions to limit the emission and enhance the capture of CO_2. Besides moving towards energy efficient applications and fostering renewable energy usage, one option in order to minimize the environmental impacts resulting from the increased levels of CO_2 is to capture it properly (Kätelhön et al., 2019; Kocs, 2017). Carbon

68 capture and storage is one of the climate change mitigation strategies currently under intense

69 consideration (Boot-Handford et al., 2013; Haszeldine, 2009), which was also outlined as

70 one of the main strategies that could limit continuous global warming (Withey et al., 2019).

71   CO_2 capture can be achieved by post-combustion, pre-combustion and air separation

72 followed by oxyfuel combustion methods (D'Alessandro et al., 2010). Due to the high

73 efficiency, low cost, and relatively low energy demand, sorption is one of the promising CO_2

74 capture methods (Zhou et al., 2017). Several physical and chemical sorption processes have

75 been extensively investigated in previous studies for CO_2 capture (Palomar et al., 2011; Sistla

76 and Khanna, 2015; Xie et al., 2017). Among those, chemical absorption using aqueous amine

77 solutions, specifically monoethanolamine (MEA) is the most commercially used method

78 (Jung et al., 2013; Lee et al., 2015; Luis, 2016). Despite that MEA is efficient and

79 economically favorable for CO_2 capture, the high energy demand, and direct and indirect CO_2

80 emissions at both downstream and upstream processes highlight the importance of seeking

81 alternative CO_2 capture strategies (Luis, 2016). To be more specific, research has shown the

82 MEA solvent regeneration step can occupy about 60% of the required energy in the CO_2

83 capture process (Kuramochi et al., 2012). Additionally, the use and generation of toxic

84 materials (e.g. ethylene oxide) during the MEA production process, increase the

85 environmental concerns in other environmental impact considerations (e.g. eco-toxicity,

86 human health, etc.). Since the use of MEA in CO_2 capture is a point of concern and a global

87 application, it may not be the optimal strategy in the long run.

88   Many advances in solid based materials for CO_2 capture have been reviewed recently

89 including solid sorbents and solid supports functionalized with amines (D'Alessandro et al.,

90 2010; Wang et al., 2014). Polymeric amines, such as polyethyleneimine (PEI), are promising

91 amine sources for CO_2 capture due to their higher amine group density compared to other

92 amine-containing compounds (Choi and Choi, 2018; Min et al., 2018a). In addition, amines

4

93   bonded to high surface area supports including metal oxides, zeolites, and carbon-based

94   materials are promising adsorbents because they offer low energy solutions for regenerable,

95   low cost, efficient and selective CO_2 capture (Liu et al., 2011). As a support, metal oxides are

96   cost-effective, easily modified, provide avenues for mesoporous hierarchical structure, and

97   allow both covalent and physical grafting of amines to the surfaces, but are susceptible to

98   thermal degradation and often undergo self-catalyzed oxidation of amines at moderate

99   temperatures resulting in lower CO_2 sorption efficiency. Zeolites have previously been

100   functionalized with amines (Cavenati et al., 2004); however, the small pore size often limits

101   the amount of amine that can be loaded onto the material, and the synthesis method often

102   impacts not only the loading of amine, but also the distribution and availability of sites. Metal

103   organic frameworks have arguably been quite efficient at CO_2 adsorption at low temperatures

104   and pressures; however, they are often prohibitively expensive to make and susceptible to

105   poor gas adsorption selectivity upon exposure to water vapor (Zhou et al., 2017). With high

106   durability, physical and chemical stability, large surface areas for adsorbate molecules, high

107   micropore volume, and relatively low cost, carbon nanotubes (CNT) are preferable support

108   materials for amines as adsorbents for post-combustion CO_2 capture (Min et al., 2018b).

109   CNT have strong electrical, chemical, thermal and mechanical properties (Abdalla et

110   al., 2015; Zhang et al., 2013). In addition, the physicochemical properties of CNT are

111   maintained under flue gas conditions due to their hydrophobicity as well as chemical and

112   thermal stability. Given that CNT are porous materials and have hollow structures, these

113   properties make them favored geometric structures for both inside and outside adsorption

114   (Boot-Handford et al., 2013). Meanwhile, CNTs are hydrophobic therefore they are resistant

115   to water vapor, which makes them more durable than other alternatives (Ganesh, 2013; Osler

116   et al., 2017). Several studies use multi-wall (MW) CNT and amine modified MWCNTs as

117   adsorbents for CO_2 capture (Jin et al., 2013; Keller et al., 2019; Lee et al., 2015). Previous

studies showed a comparable adsorption capacity of CNT-PEI compared to current MEA (30% weight) adsorption. It has been also suggested that CNT supported amine for CO_2 capturing is stable, requires much less energy for the desorption, and has a similar CO_2 capture capacity even comparable to the traditional MEA method at laboratory scale (Zhou et al., 2017).

Many novel materials with high efficiency and stability are developed recently for CO_2 capture purposes. However, the material syntheses phase also involves high energy inputs, which generates CO_2 emissions. Although solid amine using CNT as novel adsorbent materials imply high capability in CO_2 capture, the impacts of material preparation, usage and disposal on the overall environment is rarely studied. Meanwhile, large quantities of electricity are used to provide thermal and kinetic energy during the materials preparation and carbon regeneration phase, which are potential environmental burdens that could be overlooked. This study first investigates the environmental impacts of two CNT supported PEI, physiosorbed (Phy-CNT-PEI) and covalently bound (Cov-CNT-PEI) synthesized at laboratory scale, using life cycle assessment (LCA). After that, the carbon payback period and economic payback are analyzed for Phy-CNT-PEI and traditional MEA methods (Figure 1). The goal of this study is to understand the life cycle impacts of CNT-PEI synthesis as novel CO_2 adsorbents, and also gain further understanding on the potential environmental benefits and tradeoffs during the use phase. Ultimately, this study aims to identify the potential limitations and applicability of novel CO_2 capture technologies.

2. Methods and modeling

This study serves as a case study to illustrate the major challenges that solid amine as a novel CO_2 capture technology encounters in cleaner production. The methods and modeling

141   section is divided into two parts: life cycle assessment and carbon payback analysis. Figure 1
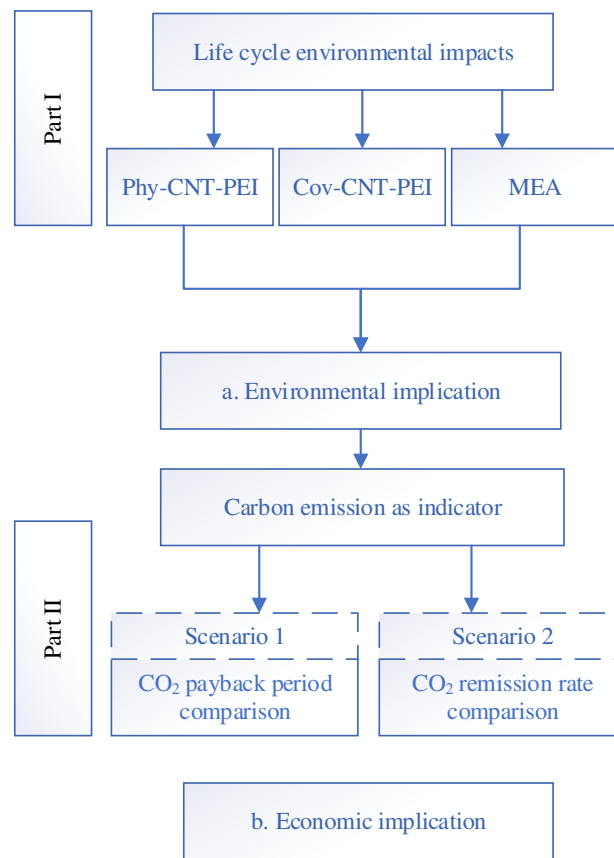
142   illustrates the flow of current research.

143

144   *Figure 1. Flow diagram illustrates the study.*

145

146   ***2.1 Life cycle assessment***

147   *2.1.1 Goal and scope*

148   The goals of this research are to investigate the environmental impact profiles of two

149   laboratory synthesized CNT-PEI, identify the hotspots and gain understanding on the

150   potential carbon payback period for different CO_2 capture methods. The environmental

151   impacts of both types of CNT-PEI syntheses were assessed initially using LCA. LCA is a

152   systematic tool for determining the environmental impacts (using metrics such as kilograms

153   of carbon dioxide emitted) of a product or process across its entire life cycle or a portion of

154   its life cycle (Finnveden et al., 2009; Klöpffer, 1997). The system boundaries are depicted in

155   Figure 2. Two functional units were used for initial direct comparison, 1 kilogram (kg) of

156   material synthesis cost (mass-based), and materials required to adsorb 1 kg CO_2. Adsorption

157   capacities are summarized in Table 1.

158

159   a. Phy-CNT-PEI
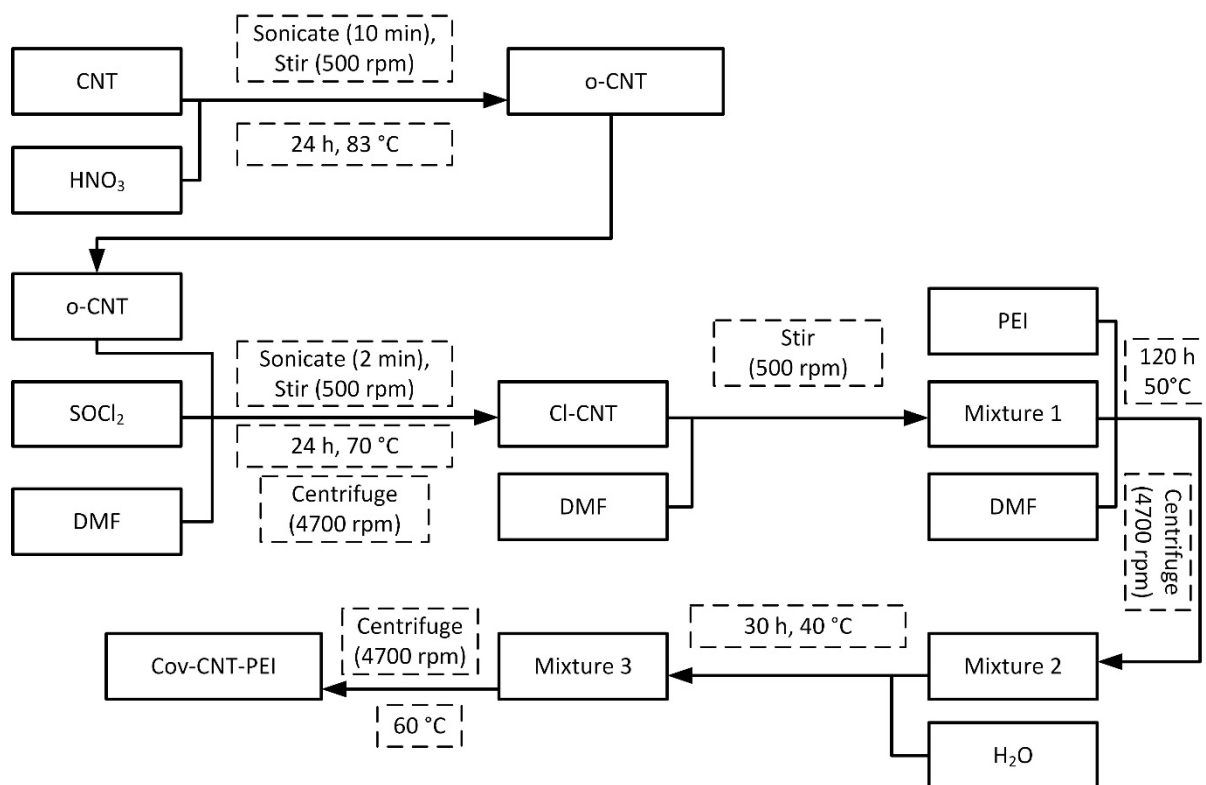

160

161   b. Cov-CNT-PEI

162
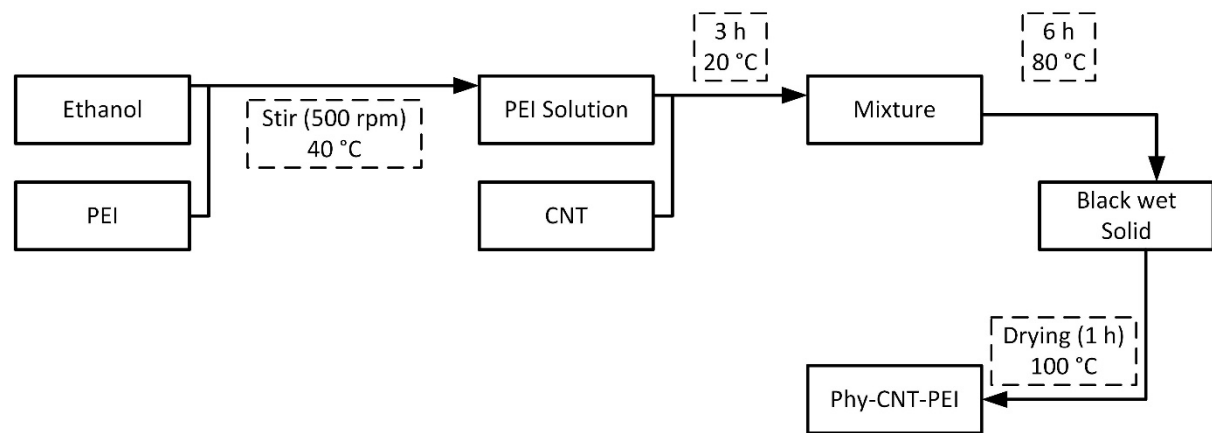
Figure 2. System boundaries and schematics of CNT-PEI (covalent & physical) syntheses
(additional syntheses, including CNT, PEI, DMF, are illustrated in the SI). CNT, PEI and
DMF are denoted as carbon nanotube, polyethyleneimine and dimethylformamide,
respectively.

Table 1. Summary of the initial CO_2 adsorption capacity for each adsorption/desorption (A/D)
cycle. Dry condition: introducing CO_2 at a flow rate of 10 $mL·min^{-1}$ with 40 $mL·min^{-1}$ N_2.
Wet condition: 3 H_2O steam by volume was introduced in the system by bubbling 40
$mL·min^{-1}$ N_2 into H_2O bath. CO_2 flow rate is still 10 $mL·min^{-1}$.

Type of material	Capacity (mmol/g)		kg CO_2/kg material	
	Dry	Wet	Dry	Wet
Cov-CNT-PEI	0.98	1.12	0.04	0.05
Phy-CNT-PEI	6.18	0.3	0.27	0.01
MEA	6.82		0.30	

173

2.1.2 Life cycle inventory

Information on materials and reagents used for the laboratory syntheses was from

Zhou *et al* (2017). The CNT used here was synthesized through the chemical vapor

9

deposition (CVD) method, which has also been identified as one of the most utilized methods

for industrial growth of carbon nanotubes (Kushnir and Sandén, 2008; Zhang et al., 2011). In

this study, materials and energy inputs were collected from a pilot scale multi-wall CNT

(MWCNT) production plant (Table S1&S2) (Fan et al., 2006). The life cycle impacts of the

MWCNT in this study was also compared to a suite of other MWCNT synthesis studies to

understand the relative impact of the production scale.

Due to the limited information from the chemical vendor, PEI synthesis procedures

were obtained from multiple literature sources (Bieber and Elsässer, 2001; Chaikittisilp et al.,

2013; Tauhardt et al., 2011). The flow chart of PEI synthesis and material inputs are

presented in Figure S1 and Table S3&S4, respectively. Materials and energy inputs for

synthesizing both CNT-PEI are listed in Table S5&S6. The electricity and energy usage to

produce CNT-PEI were either collected directly from the laboratory equipment, or estimated

based on the first law of thermodynamics (equations S1 and S2) when the materials were not

synthesized on-site (Wu et al., 2019). Detailed equations and numbers are presented in the

supporting information (SI).

2.1.3 Life cycle impact assessment and interpretation

The life cycle environmental and human health impacts were modeled using the

SimaPro software (version 8.5) with Ecoinvent and USLCI (U.S. Life Cycle Inventory)

databases as inventories (Wernet et al., 2016). SimaPro is one of the most widely used LCA

softwares, which provides a modeling environment from simple to complex products or

systems. TRACI 2.1 (tool for the reduction and assessment of chemical and other

environmental impacts) was used as the assessment method to represent an United States

based study (USEPA, 2012). The midpoint categories considered include ozone depletion

201   (OD; kg CFC-11 equivalent), global warming (GW; kg CO_2 eq), smog (PS; kg O_3 eq),

202   acidification (AC; mol SO_2 eq), eutrophication (EU; kg N eq), carcinogenic (HHC; CTUh),

203   non-carcinogenic (HHNC; CTUh), respiratory effects (RE; kg PM2.5 eq), ecotoxicity (EC;

204   CTUe), and fossil fuel depletion (FF; MJ surplus) (Wu et al., 2019).

205

206   *2.1.4 Sensitivity and uncertainty analysis*

207   Sensitivity analysis determines the output parameter percentage change by varying an

208   individual input parameter, while all the other parameters are constant (Stoykova, 2010),

209   which shows the influence of one parameter (the independent variable) on the value of

210   another (the dependent variable). In this case, the purpose of the sensitivity analysis is to

211   monitor how sensitive of each synthesis procedure is to the overall CNT-PEI production.

212   Therefore, the sensitivities of CNT-PEI syntheses were assessed by varying a single

213   parameter value (increased by 25%), and compare the change of the overall impact for each

214   impact category. The uncertainties associated with the unit processes in the life cycle

215   database were analyzed using Monte-Carlo simulations in SimaPro for 1000 runs to the 95th

216   confidence interval.

217

218   **2.2 Carbon payback analysis**

219   As the targeted application of the studied technology is to store CO_2, global warming

220   potential was selected as a major indicator to analyze the environmental payback in this study.

221   The concept of environmental payback is well established and has been used to compare the

222   relative environmental impact of numerous conventional and emerging technologies,

223   particularly in energy applications such as fuels and photovoltaics (Gibbs et al., 2008; Jonker

224   et al., 2014; Rankine et al., 2006). Here, the carbon payback is calculated as the number of

225   adsorption/desorption (A/D) cycles required to obtain CO_2 saving equivalent to the initial

226   CO_2 cost, which is generated from the material syntheses. The carbon paybacks of carbon

227   capture technologies were compared with a commonly adapted MEA strip method to gain

228   further understanding on the potential of application.

229   The summaries of CO_2 adsorption capacity under varying scenarios are presented in

230   Table 1. From previous experiments, results suggest that Cov-CNT-PEI has a higher CO_2

231   adsorption capacity than Phy-CNT-PEI under wet adsorption scenario, whereas the CO_2

232   adsorption capacity for Phy-CNT-PEI is much higher under dry condition than Cov-CNT-PEI,

233   and similar to MEA (Zhou et al., 2018, 2017; Zoannou et al., 2013). Most industrial CO_2

234   exhaust streams are generated in post-combustion processes, where the concentration of CO_2

235   in the gas mixture ranges from 3-20% by volume (Markewitz et al., 2012). Therefore, the

236   CO_2 concentration used in the adsorption capacity test was 20% in N_2 by volume. Phy-CNT-

237   PEI under dry condition was investigated further for the environmental payback comparison

238   due to the comparatively high adsorption capacity. Two scenarios were considered to

239   evaluate the carbon payback of the targeting technology.

240

241   *2.2.1 Scenario 1: CO_2 payback period comparison*

242   In scenario 1, the number of A/D cycles required to match with the initial MEA and

243   CNT-PEI CO_2 cost during syntheses are calculated. The net amount of CO_2 remission by 1 kg

244   of adsorbents are expressed as equation 1.

245   Life time CO_2 remission $= \sum_{K=0}^{n}(K - D) - I$ (equation 1)

246   In which, K represents the CO_2 adsorption after corresponding cycle (kg CO_2), and D

247   represents the CO_2 generated from the desorption energy use (kg CO_2). $(K-D)$ represents the

248   net gain of CO_2 remission for each corresponding cycle. *I* represents the initial synthesis cost

249   (kg CO_2).

250

251   *2.2.2 Scenario 2: CO_2 remission rate comparison*

252   The rates for CO_2 remission between Phy-CNT-PEI and MEA were compared in

253   scenario 2. More industrial relevant approach was considered by replenishing fresh MEA

254   once the capacity decrease to a certain level. During industrial application, the CO_2

255   adsorption capacity should be maintained at a relatively stable level. Since liquid MEA can

256   degrade after each A/D cycle, MEA was replenished when the adoption capacity is decreased

257   to 95% of the original capture capacity (which equals to every 10 cycles). No replenishing or

258   replacement was considered for CNT-PEI due to their stability nature.

259

260   **3. Results and discussion**

261   The results are presented in the following order: life cycle impact comparison

262   between two CNT-PEI syntheses with different functional units (Figure 3); impact

263   contribution for two CNT-PEI synthesis (Figure 4); carbon emission for synthesizing 1 kg of

264   each absorbent (Figure 5); carbon payback analysis: scenario 1 and scenario 2 (Figure 6 and

265   Figure 7).

266   ***3.1 Life cycle impact of CNT-PEI production***

267   *3.1.1 Impact comparisons between two types of CNT-PEI*

268   Figure 3 shows the relative environmental impacts comparison between Phy-CNT-

269   PEI and Cov-CNT-PEI by using two different functional units. When the mass based

270   functional unit was used, the environmental impacts generated from synthesizing Phy-CNT-

271   PEI were ranged from 40-80% compared to Cov-CNT-PEI in all impact categories,

272   suggesting that the Phy-CNT-PEI has low environmental burdens during synthesis phase.

273   Only the consideration of mass may not accurately estimate the impact of CNT-PEI with

274   respect to the utility of CO_2 remission. The functional units should specifically focus at the

275   targeted material function, which in this case, amount of CO_2 adsorption was added as the

276   additional functional unit for comparison. When the results were rescaled based on the CO_2

277   adsorption efficiency, Cov-CNT-PEI showed even higher impacts, with nearly 10 times

278   higher impacts than Phy-CNT-PEI (Figure 3b). This is mainly due to the lower CO_2

279   adsorption capacity in Cov-CNT-PEI than Phy-CNT-PEI. The CO_2 adsorption capacity of

280   Phy-CNT-PEI is nearly 6 folds higher than Cov-CNT-PEI under dry CO_2 condition (Table 1).

281   From the previous material characterization on both types of CNT-PEI, it shows that 40%

282   PEI was physically adsorbed on CNT (Phy-CNT-PEI), whereas only 16% PEI was covalent

283   bound to CNT (Cov-CNT-PEI). Therefore, improve amine group that bound to CNT could

284   potentially enhance their CO_2 capture capacity, meanwhile decrease the corresponding

285   environmental burdens generated from material production. Overall, both functional units

286   illustrate that the Cov-CNT-PEI has higher overall impacts than Phy-CNT-PEI.

287

a. Synthesis 1 kg material based function unit

b. Adsorb 1 kg CO_2 based fuction unit
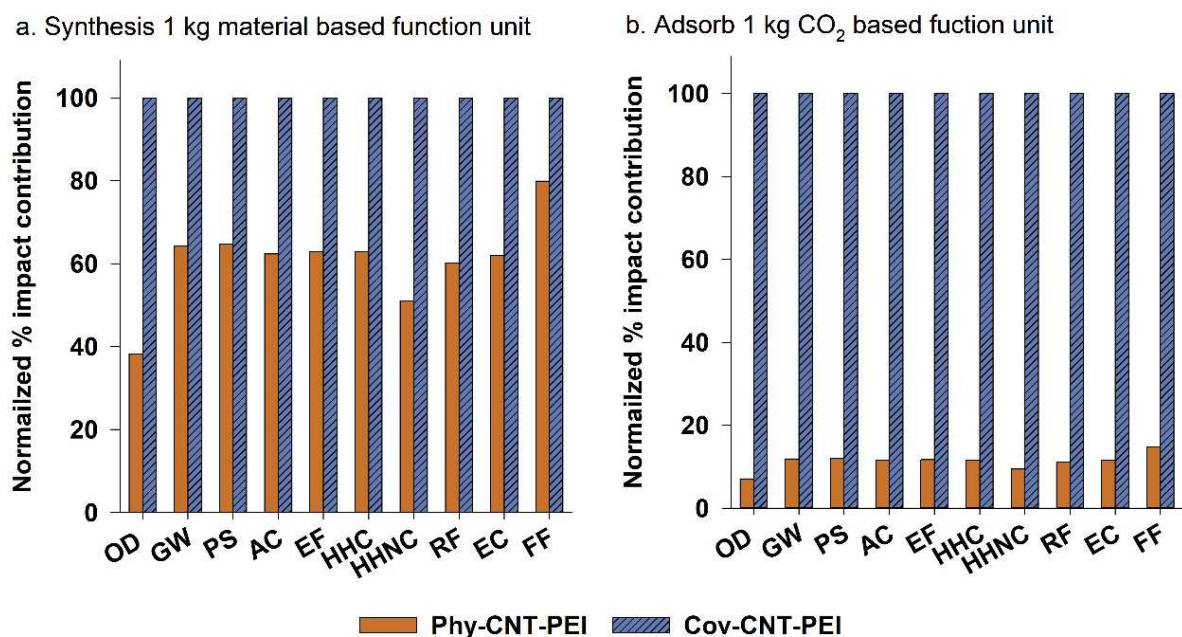
Phy-CNT-PEI   Cov-CNT-PEI

Figure 3. Normalized percent impact for all assessed categories by comparing both CNT-PEI when (a) synthesis 1 kg CNT-PEI and (b) adsorb 1 kg CO_2 as function unit, respectively. Ozone depletion (OD), global warming (GW), smog (PS), acidification (AC), eutrophication (EU), carcinogenic (HHC), noncarcinogenic (HHNC), respiratory effects (RE), ecotoxicity (EC), and fossil fuel depletion (FF).

3.1.2 Impact contributions of each procedure

Figure 4 illustrates the environmental impact contributions of each main procedure during both CNT-PEI syntheses. In Figure 4a, CNT manufacturing is the driving environmental burden in all impact categories, it contributes more than 50% of environmental burdens to all the categories due to its intense synthesis condition such as high temperature and large amount of feedstocks (Figure S5). PEI synthesis was identified to be the second largest contributor (~20%). Compared to the materials, the contribution by electricity consumption is negligible in Phy-CNT-PEI. For Cov-CNT-PEI, additional chemical compounds (i.e. DMF, thionyl chloride) were involved in the synthesis to form strong covalent bonds between the CNT and PEI, which generate additional environmental burdens due to the large quantity being utilized (Figure 4b).

Furthermore, the sensitivity analyses for both CNT-PEI syntheses are listed in Table S15&S16. Results show that CNT and PEI syntheses are the most sensitive parameters during material synthesis throughout life cycle, which again confirms that the CNT and PEI production dominate the environmental impacts in the both CNT-PEI syntheses. Additionally, the use of organic compounds, especially thionyl chloride ($SOCl_2$) and dimethylformamide (DMF) showed high sensitivity to the impacts associated with Cov-CNT-PEI. The associated uncertainties around both CNT-PEI syntheses were analyzed and revealed to be low (Figure S4). The environmental impacts related to all materials synthesis are tabulated in Table S7-S14, and the environmental impact contributions are graphically presented in Figure S5-S8.
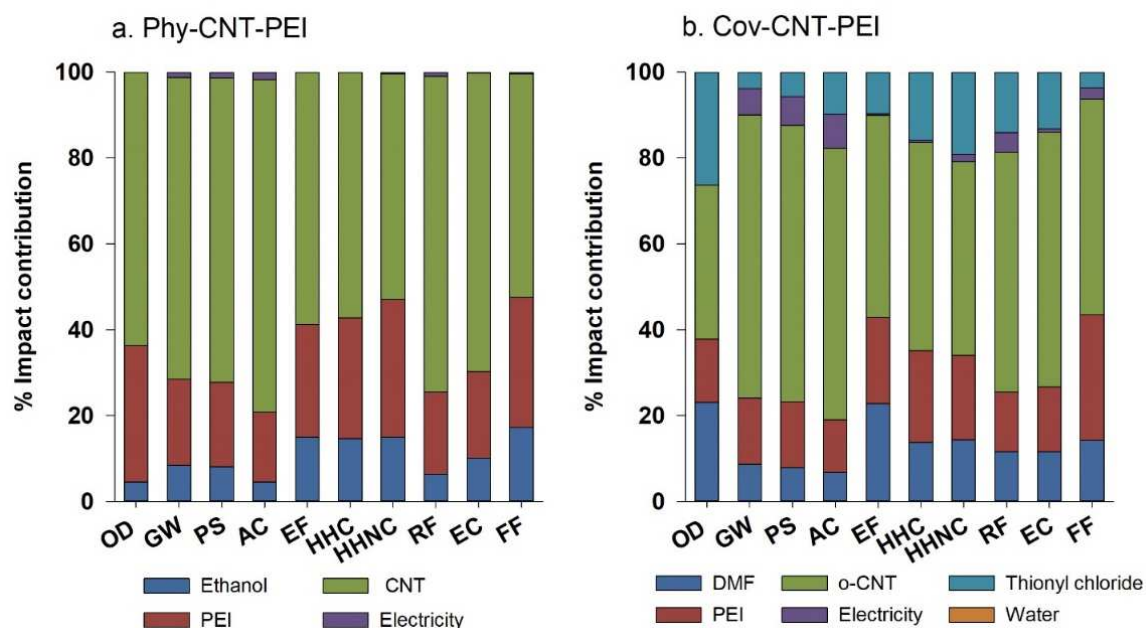
Figure 4. Impacts contribution during CNT-PEI syntheses. a) impact contribution of Phy-CNT-PEI; b) Cov-CNT-PEI. (higher categories normalized as 100%). Ozone depletion (OD), global warming (GW), smog (PS), acidification (AC), eutrophication (EU), carcinogenic (HHC), noncarcinogenic (HHNC), respiratory effects (RE), ecotoxicity (EC), and fossil fuel depletion (FF).

By using global warming potential as an indicator, Figure 5 illustrates the CO_2 produced through the manufacturing of 1 kg of adsorbent. MEA requires much less materials and energy input than CNT-PEI due to their industrial scale manufacture. The CO_2 generation associated with CNT-PEI syntheses are 72 (Phy-CNT-PEI) and 113 (Cov-CNT-PEI) times higher than MEA. CNT contributes over 50% of GW to the overall production process in both CNT-PEI. Meanwhile, Cov-CNT-PEI generates more GHG emission than Phy-CNT-PEI, largely attributed to the pre-treatment of CNT (for creating covalent bonds) and organic chemical compounds (e.g. DMF) used.
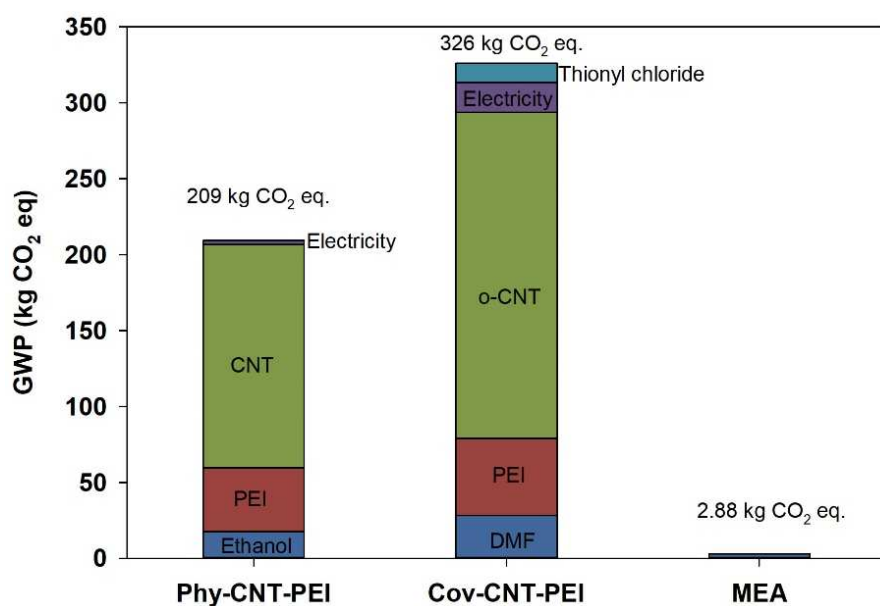
329

Figure 5. Quantity of CO_2 generated by synthesizing 1 kg of Phy-CNT-PEI, Cov-CNT-PEI,
and MEA. Color schemes represent the materials and processes contribution in each type of
product synthesis. GWP: global warming potential.

3.1.3 Major GW contributor and implication

Life cycle inventory for CNT production were compiled based on a pilot scale

manufacturing plant (up to 20 g MWCNT/h) (Fan et al., 2006). LCA analysis indicates

supporting gas and electricity are the two major contributors for the overall CNT production

(Figure S6). Especially for GW impact category, electricity contributed over 80% of the

greenhouse gas emission. Other LCA research also investigated the environmental impacts of

CNT syntheses under laboratory conditions, and identified the largest impact was due to the

energy consumption, followed by the equipment infrastructure (Griffiths et al., 2013). Thus,

converting to cleaner energy sources may decrease future CO_2 emissions associated with the

environmental manufacturing cost. For PEI and other chemical syntheses, material usage,

including organic and inorganic chemicals, and electricity dominated the environmental

impacts for the production (Figure S6-S8).

346　　　　Although environmental impact results analyzed based on laboratory scale production

347　　cannot be scaled up directly, it is helpful to identify the energy and material intensive

348　　processes, and to minimize the corresponding cost and lower the associated environmental

349　　impacts before scaling up. In addition, it provides the maximum environmental impacts

350　　possible during the material synthesis phase, which generates the most conservative

351　　comparison in CO_2 paybacks to our study.

352　　　　It has to be recognized that scale up from laboratory level to pilot scale can potentially

353　　save materials and energy sources due to higher reaction yields, recycling of reagents and

354　　efficient equipment (Gao et al., 2013). Research also suggests scaling up the process could

355　　potentially save up to 6.5 times more material and energy inputs than a typical laboratory

356　　synthesis (Piccinno et al., 2018). Compared to other laboratory scale CNT syntheses, results

357　　using a pilot plant data generated up to 40 times less CO_2 emission than the most intensive

358　　chemical vapor deposition method (Figure S2). Since industrial scale production could

359　　further decrease the corresponding environmental impacts by improving the materials and

360　　energy efficiency, there still is a large potential for lowering the associated environmental

361　　burdens for PEI-CNT to be manufactured when scaling up.

362

363　　*3.2 Carbon payback comparison*

364　　　　Although CNT-PEI shows large CO_2 cost during synthesis, the high stability and

365　　consistency in CO_2 remission overtime provides potential for them to achieve environmental

366　　benefits in the long run. Thus, the carbon payback of Phy-CNT-PEI was analyzed and further

367　　compared with MEA.

368　　*3.2.1 Scenario 1: CO_2 payback period comparison*

369   Table 2 summarizes the net CO_2 remission between 1 kg of Phy-CNT-PEI and MEA

370   during one A/D cycle. Phy-CNT-PEI saves up to 60% energy demand compare to the MEA

371   method for each A/D cycle due to its lower heat capacity. With a lower CO_2 remission

372   capacity, Phy-CNT-PEI still shows a similar net CO_2 remission per cycle compared with

373   MEA, due to the lower energy required per A/D cycles. This is also a benefit of utilizing

374   solid supported amine for CO_2 capture due to the low heat capacity compared to liquid phase

375   materials.

376
377   *Table 2. Comparison of the net CO_2 remission between Phy-CNT-PEI and MEA.*
378

Type of material	Heat capacity (KJ/kg-K)	kg CO_2 saving/kg of Product	Energy required/cycle (KJ)	Corresponding CO_2 produced/cycle (kg)	Net CO_2 remission/cycle (kg)
Phy-CNT-PEI	1.40	0.27	70.20	0.02	0.26
MEA	3.46	0.30	172.85	0.04	0.26

379

380   CO_2 payback period of utilizing 1 kg MEA and Phy-CNT-PEI are calculated (based

381   on equation 1) and compared in Figure 6. For MEA, the maximum CO_2 capture has been

382   modeled to be 11.76 kg after considering the degradation (Figure 6a). Since the CO_2 cost for

383   manufacturing 1 kg MEA equals to 2.88 kg CO_2, the net cumulative CO_2 remission is 8.88 kg

384   CO_2/kg MEA. The CO_2 payback period is estimated to be 21 A/D cycles. There will be no

385   CO_2 saving after 176 cycles because the amount of CO_2 generated from the desorption

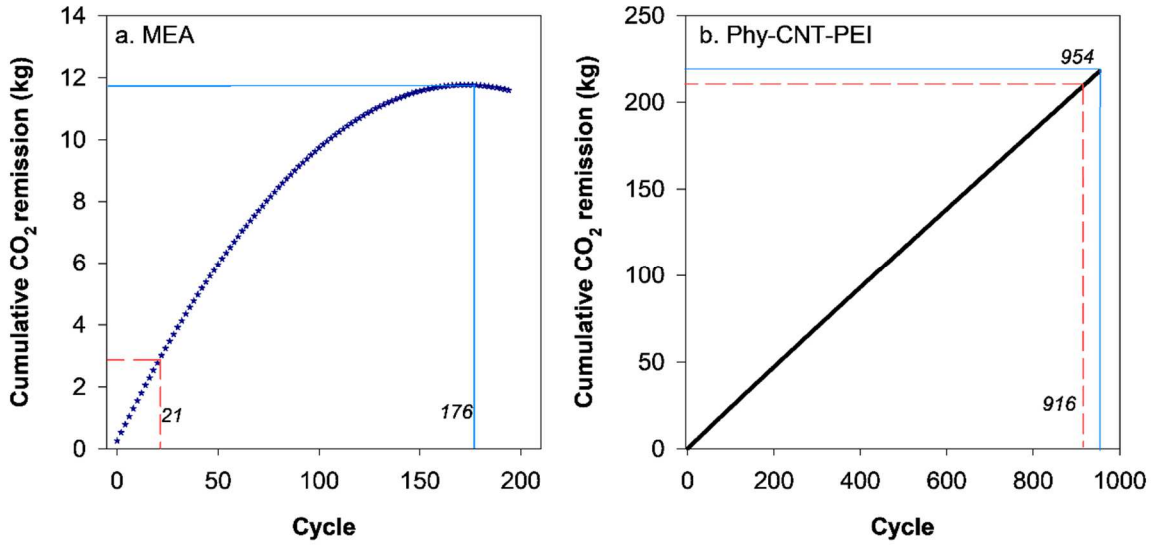386   process is higher than the remission savings.

387

Figure 6. Lifetime cumulative CO_2 remission and payback cycles for MEA (a) and physiosorbed CNT-PEI (b) (scenario 1). Red dash line in both panels indicates the corresponding CO_2 payback after cycles of use. Blue solid line in panel a indicates the lifetime payback and cycles of use for MEA, in panel b indicates the cycles required to remediate the same quantity of CO_2 compared to MEA.

393

394   For Phy-CNT-PEI, the cumulative CO_2 remission tends to follow a linear trend

395   because of the slow degradation rate and relative stable CO_2 recovery capacity over cycles.

396   However, Phy-CNT-PEI has a nearly 72 times higher initial manufacturing CO_2 cost than

397   MEA, with 209 kg CO_2 generation when synthesizing 1 kg Phy-CNT-PEI (Figure 5). The

398   initial CO_2 cost requires an estimate of 916 A/D cycles to obtain a payback breakeven point

399   (Figure 6b). Due to the relatively high and stable CO_2 capacity, only additional 38 A/D cycles

400   (954 in total) reach equivalent lifetime CO_2 remission with 1 kg MEA.

401

402   *3.2.2 Scenario 2: CO_2 remission rate comparison*

403   Research indicates that MEA can be degraded to other products with much lower CO_2

404   adsorption capacity, such as 2-oxazolidone, N-(2-hydroxyethyl)-ethylenediamine, and 1-(2-

405   hydroxyethyl)-2-imidazolidinone over time (Zoannou et al., 2013). During this 8 weeks study,

20

406   the thermal degradation of MEA has shown a reduction by 95% at 160 ℃ (Zoannou et al.,

407   2013). Another study showed a MEA degradation by 2.5 to 6% every 2-week cycles (Davis

408   and Rochelle, 2009). In contrast, the recovery rate of CNT-PEI has been proven to be much

409   higher and more stable than MEA. CNT-PEI has previously been proven experimentally to

410   maintain a stable recovery rate up to 100 cycles (Su et al., 2014). Su *et al.* also showed a slow

411   degradation for CNT-PEI, where recovery after 1, 50, and 100 A/D cycles are 100, 94.37, and

412   92% (2014). The CO_2 adsorption capacity for Phy-CNT-PEI and MEA through cycles were

413   fitted with an exponential and linear decay curve, respectively. The exponential decay curve

414   (equation 2) was fitted following a recovery study conducted by Zhang *et al.* (2012). They

415   showed a 10-cycle data points including the initial state and the steady state during the

416   capture process (Zhang et al., 2012). In order to accurately estimate the material stability for

417   CO_2 capture, the data was used to establish a prediction for material stability in a long-term

418   CO_2 capture. For MEA, the degradation rate was fitted using equation 3, with a conservative

419   estimation approximately 0.5% MEA loss per cycle (Davis and Rochelle, 2009). The fitted

420   models are presented in Figure S3 and S4.

421   For CNT-PEI (exponential decay):

422        $$y1 = -1.72 \times \ln(x) + 98.8 \qquad \text{(equation 2)}$$

423   For MEA (linear decay):

424        $$y2 = -0.51x + 99.9 \qquad \text{(equation 3)}$$

425   In equations 2 and 3, $y1$ and $y2$ are the adsorption/absorption capacities of CNT-PEI and

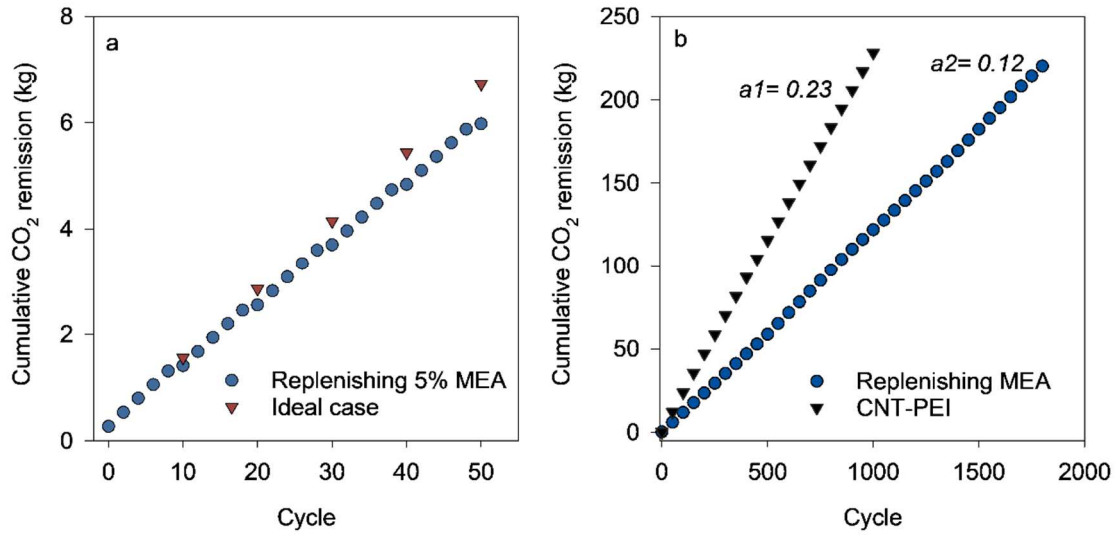426   MEA at x cycle, respectively.

427

428

Figure 7. a) Cumulative CO_2 remission when replenishing 5% MEA back after every 10 cycles (red triangle represents an ideal condition where no degradation of MEA, blue circle represents the loss of cumulative CO_2 remission after replenishing 5% MEA every 10 cycles); b) comparative cumulative CO_2 remission between replenishing MEA scenario with Phy-CNT-PEI.

In reality, replenishing degraded and lost MEA after certain cycles could maintain a consistent and stable CO_2 capture capacity. Since approximately 5% of MEA degradation is expected with every 10 A/D cycles, to maintain a consistent capture capacity, an additional 5% of MEA was replenished after every 10 cycles for comparison in this scenario. The corresponding CO_2 generation associated with the 5% MEA replenished was included as a loss for the cumulative CO_2 remission (demonstrated in Figure 7a). The results suggest that during the 10 cycles, replenishing the first A/D cycle offsets the 5% MEA CO_2 manufacturing cost. Therefore, the remaining 9 cycles are the actual net CO_2 remission.

The rate for CO_2 remission between Phy-CNT-PEI and replenishing MEA are compared in Figure 7b. Results show that Phy-CNT-PEI has a much higher CO_2 remission rate (0.23 kg CO_2/cycle) than the replenishing MEA scenario (0.12 kg CO_2/cycle). By simply assuming 1000 A/D cycles as a lifetime for CNT-PEI, the cumulative CO_2 remission in Phy-CNT-PEI at 1000 cycles are more than doubled compared to the MEA. Therefore,

22

448 operational lifetime of CNT-PEI is the determining factor and critical for the overall

449 environmental performance in CO_2 remission.

450

451 *3.3 Environmental implications*

452   Although many studies have conducted LCA on the capture of CO_2 under industrial

453 post-combustion, and have found that post-combustion CO_2 capture can decrease the global

454 warming potential (Castelo Branco et al., 2013; Young et al., 2019), there are other

455 environmental impacts associated and additional fuels demanded (Chisalita et al., 2019).

456 With the limitations of current CO_2 capture technologies, novel materials are in urgently

457 needed to improve the efficiency. Previous studies investigated the life cycle impacts of a

458 membrane separation technology, where they found membrane separation has lower life

459 cycle emissions compared to conventional MEA absorption process (Giordano et al., 2018).

460 The authors indicate that the environmental impacts are strongly related to the membrane

461 material, which is similar in our case where the materials usage are the determine factor in

462 terms of life cycle emissions. In another study, researchers used potassium carbonate as an

463 alternative for CO_2 capture, and the LCA results suggest potassium carbonate is better than

464 MEA in all environmental categories (Grant et al., 2014). Although these studies compared

465 the life cycle impacts of different carbon capture technologies, none of these considered the

466 environmental payback period from manufacturing and the environmental tradeoffs over the

467 life time. Solid amine as a novel absorbent in CO_2 capture, the life cycle emissions have not

468 been previously investigated. In addition, researchers summarize that energy penalty,

469 functional units, scale-up issues, market effects and several other issues are the major

470 challenges, which are overlooked in carbon capture and storage investigations (Sathre et al.,

471   2012). Thus, the present study attempts to serve as a case study and discuss some of the

472   current major challenges.

473   The results suggest that carbon payback analyzed in present study is largely

474   dependent on the lifetime (A/D cycles) of CNT-PEI. Although many studies only showed

475   consistent recovery rate up to 100 cycles, our results indicate that a total of 912 A/D cycles

476   are required to be able to obtain a breakeven CO_2 payback for Phy-CNT-PEI (Figure 6b).

477   Currently, very limited number of studies reported the actual lifetime and the A/D cycles of

478   CNT-PEI that can be achieved. Begag *et al.* studied the capacity of a solid state amine

479   (amine-functionalized aerogel) over 2000 A/D cycles in a fixed bed (Begag et al., 2013).

480   They found that the capacity was decreased by only a small amount (from 1.5 to 1.4 mmol

481   CO_2/g sorbent) over such a large number of cycles (Begag et al., 2013). This study provides

482   evidence suggesting solid state amine should have a long lifetime to achieve environmental

483   benefits. In addition, to optimize the synthesis procedures and enhance the CO_2 adsorption

484   capacity, future research should also investigate and ensure the maximum lifetime capacity of

485   current CNT-PEI under extreme conditions in order to receive more concise payback

486   outcomes. Importantly, this present study simplifies the A/D process by assuming no

487   additional adverse environmental impact caused by the degradants of MEA. In reality, MEA

488   degradants can also dilute the MEA concentration, which decrease the CO_2 capture capacity.

489   These technical challenges minimize the benefits of liquid phase capturing technologies, and

490   highlight the benefits of developing solid supported amine for CO_2 remission.

491   Although research related to solid state amines for CO_2 capture is still in the early

492   stage and many technical challenges needed to be overcome, solid state amines have become

493   more attractive in CO_2 capture recently since the technology is solvent free (Min et al.,

494   2018a), which reduces the energy penalty from regeneration compared to traditional liquid

495   capture methods (Table 2). However, the large energy requirement for the adsorbent

496 preparation (production and characterization) is still an issue that can almost counteract the

497 energy requirement for regeneration. Substantial studies should be conducted to optimize the

498 reduction of energy required in adsorbent preparation, improvement of adsorbent stability

499 (e.g. thermal and steam) and CO_2 capture capacity under realistic flue gas conditions

500 (D'Alessandro et al., 2010). Moreover, reactor and process design should be optimized for

501 solid state amines since very few publications are involved in this field (Dutcher et al., 2015).

502

503 *3.4 Economic implications*

504 From a business perspective, the cost of reducing emissions should be taken into

505 account when making economically sustainable decisions (Schwartz et al., 2020). Table 3

506 shows the estimated price for CO_2 adsorbents and electricity used per cycle based on the

507 material flow. For the synthesis of 1 kg Phy-CNT-PEI, 0.6 kg CNT, 0.4 kg PEI and 50 kg

508 ethanol was used. Ethanol was recycled during syntheses and adjusts the total cost of

509 manufacturing 1 kg Phy-CNT-PEI at $580. CNT contributes 72% of the cost.

510 Monoethanolamine (MEA, 98%) has been commercialized and can be directly purchased

511 with the price of $40/kg. Since the concentration of MEA is 30% in the industrial CO_2

512 capture and thus the price can be adjusted to $12/kg. The syntheses cost of Phy-CNT-PEI is

513 48 times higher than MEA. However, since MEA suffers from chemical degradation and

514 caused equipment erosion, additional material usage and maintenance are required. In

515 addition, extra electricity will be consumed each desorption cycle, the energy cost of MEA is

516 2.5 times higher than Phy-CNT-PEI. Although Phy-CNT-PEI shows benefits in costs during

517 the use phase, the high synthesis cost limits the widespread industrial application. The total

518 cost of Phy-CNT-PEI can be reduced to be the same as MEA after 8900 cycles. By

519 integrating economic analysis, energy stakeholders and general public would gain better

520 interests towards environmental technologies in the future research (Sun et al., 2020).

521   It is relevant to note that it is an overestimation based on the assumptions such as

522 laboratory scale and high grade of chemicals used for CNT-PEI. However, from the

523 economic point of view, traditional MEA remains to be a better alternative for industrial

524 application. Same as the environmental payback outcomes, decreasing the CNT and other

525 material costs will benefit the application of solid amine adsorbents in CO_2 capture.

526 *Table 3. Summary of the CO_2 adsorbents price and electricity used per cycle. Detailed*
527 *material price are presented in Table S17.*

Type of material	Market price ($/kg)	Energy (kWh/cycle)	Mean price ($/cycle)
Phy-CNT-PEI	580	0.02	0.0026
MEA	12	0.05	0.0064

528

529   In general, CO_2 capture phase contributes 70% - 80% of total costs during carbon

530 capture and strange (Lee and Park, 2015), therefore, develop novel CO_2 sorbents that satisfy

531 technical and economic needs is the ultimate goal to achieve sustainability. Metal oxides,

532 such as alumina, have low production cost, but easy to corrode over time could enhance the

533 maintenance cost dramatically, meanwhile, high energy consumption during CO_2 desorption

534 indicates an overall low sustainability. Zeolites, silica materials, and metal organic

535 frameworks are known for their poor economic efficiency due to high production cost.

536 Especially for metal organic frameworks, which typically cost serval thousand dollars per

537 kilogram, therefore limit the application at larger scales (Lee and Park, 2015). In addition,

538 other carbon-based materials such as carbonaceous materials, are potential alternatives for

539 CO_2 capture. They are thermal and steam stable, with reasonable production cost, and low

540 energy consumption in the desorption process. Although the cost and the economic

541　implication of these alternatives have not been investigated extensively. In addition to the

542　environmental burdens generated during materials production, the economic efficiency of

543　alternative materials should be considered and investigated thoroughly for the future work to

544　benefit decision making.

545

4. Conclusions

547　　　Many researchers develop novel CO_2 capture adsorbents generally put emphasis on

548　improving adsorption efficiency and stability during the capture processes. However, the

549　environmental burdens generated through material syntheses and utilization are largely

550　overlooked. Our study serves as an example, to investigate the environmental impacts of

551　solid amine as a carbon capture application, and performed environmental and economic

552　trade-off comparisons with a traditional carbon capture method for the first time. The key

553　findings of this study are:

554　　　1) CNT-PEI as a solid amine absorbent, showed much higher environmental costs

555　than the traditional MEA method during their initial manufacturing phase. CNT production

556　identified as the major contributor during the life cycle environmental impacts. There is still

557　potential to optimize current technology, such as using more sustainable energy source,

558　scaling up and recycle to enhance the production efficiency.

559　　　2) The carbon payback period for Phy-CNT-PEI are 917 cycle. With higher CO_2

560　remission rate, consistent capture capacity and reusability, Phy-CNT-PEI provided great

561　potential to overcome some barriers such as offset CO_2 cost and increase the sustainability of

562　current CO_2 capture techniques, however, high initial environmental and economic costs do

563　not favor CNT-PEI to be used in industrial application with current performance.

564   Given that CO_2 emission plays a major role in global climate change, developing

565   novel technologies that mitigate CO_2 emissions is critical. However, when implementing a

566   novel technology, the corresponding environmental impacts associated should be taken into

567   consideration. Our study highlights that unilateral emphasis of the CO_2 capture efficiency by

568   novel materials is not enough, comprehensive environmental and economic impact

569   comparisons throughout material life cycles should be investigated. In this study, an

570   understanding of hotspots in the material life cycle allows researchers and developers to work

571   towards optimizing the production processes (CNT and PEI syntheses in the present study),

572   and to limit negative environmental impacts that may be associated with CNT enabled

573   adsorption technologies. In addition, future development for solid amine adsorption that

574   enhances the CO_2 remission capacity and extends product lifetime are important in making

575   this technology more valuable and competitive.

576

577   **Conflicts of interest**

578   There are no conflicts of interest to declare.

579

585

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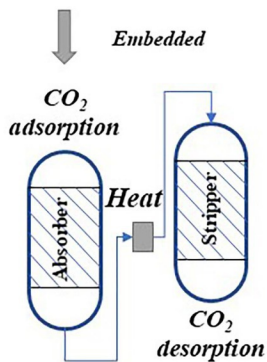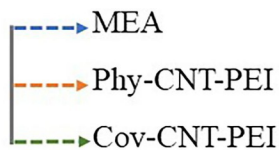
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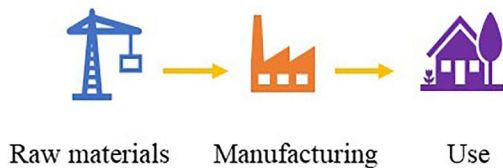
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774

CO$_2$ capture materials

- MEA
- Phy-CNT-PEI
- Cov-CNT-PEI

Embedded

CO$_2$ adsorption

Absorber

Heat

Stripper

CO$_2$ desorption

Life cycle impact

Raw materials → Manufacturing → Use

CO$_2$ payback period

Initial CO$_2$ cost

Amount of CO$_2$ saved