Environmental impact assessment of converting flexible packaging plastic waste to pyrolysis oil and multi-walled carbon nanotubes

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Abstract

A solution to low recycling rates of plastic waste is the conversion into multi-walled carbon nanotubes (MWCNTs) that have high value and can create additional revenue for plant operators. The purpose of this study was to perform a life cycle assessment (LCA) of an integrated system that involves flexible packaging plastic waste (FPPW) pyrolysis, oil upgrading, and MWCNTs production. The objectives were to determine the environmental impact of MWCNTs synthesis from non-condensable pyrolysis gases, and to assess the

environmental impact of MWCNTs synthesis from different plastic fractions. Integrating MWCNTs synthesis to the plastic pyrolysis process provides various environmental benefits including, reduction of contribution towards climate change, fossil depletion, human toxicity (cancer), and ionizing radiation potentials. Sensitivity analysis of MWCNTs yields provided the range of impacts on the environment and a critical yield of >2% for most impact categories was determined. Comparison of different plastic fractions indicated that using low PET content feedstock had lesser impact on the environment, and demonstrated comparable performance to mixed virgin plastics for most impact categories. The results highlighted the versatility of the integrated pyrolysis process for treating diverse plastic waste fractions with negligible effects from the impurities present in the actual FPPW during thermal processing.

Keywords: LCA, plastic waste, carbon nanotubes, pyrolysis, environmental impact

Nomenclature

FPPW	flexible packaging plastic waste
MWCNTs	multi-walled carbon nanotubes
LCA	life cycle assessment
FU	functional unit
PE	polyethylene
PP	polypropylene

PET	polyethylene terephthalate
PET-12	PET content 11.8%
PET-28	PET content 27.5%
MVP	mixed virgin plastics
PS	polystyrene
CCVD	catalytic chemical vapor deposition
HHV	higher heating value
S1	Scenario 1, conversion of PET-12 to pyrolysis oil
S2	Scenario 2, conversion of PET-12 to pyrolysis oil and MWCNTs
S-A	Scenario A, conversion of PET-12 to pyrolysis oil and MWCNTs
S-B	Scenario B, conversion of PET-28 to pyrolysis oil and MWCNTs
S-C	Scenario C, conversion of MVP to pyrolysis oil and MWCNTs

1. Introduction

Globally, plastic demand has been ever increasing since its first commercial use. EU consumed 49.9 Mt of plastics in 2016 wherein the amount of collected post-consumer waste plastics was 27.1 Mt, of which 61.6% was ascertained as packaging plastic waste [1]. Contrarily, owing to high volume to weight ratio, low prices of virgin feedstock, and high costs of transportation and reprocessing, plastic waste is considered an uneconomic material for collection and recycling [2]. However, it is a significant waste stream and accounts for up to 30-35% of total municipal solid waste in industrialized countries [3]. The service life of plastics varies from less than a year to over fifty years, whereas single-use packaging plastics are often used for less than a day [1]. Recycling rate of flexible packaging plastic waste (FPPW), in particular, is insignificant due to its low recycling value, diverse material composition, and residual impurities by the packaged content. After a short first-use cycle, 95% of packaging plastic material value is obsolete to the economy [4].

Pyrolysis is a widely used technology that can process FPPW into oil, solid residues and non-condensable gases [5-8]. While pyrolysis oil can be collected and sold as a fuel, non-condensable gases are typically burnt [9, 10], contributing to CO_2 emissions. Recently, several studies proposed to utilize this gas stream for the synthesis of carbon nanomaterials, such as multi-walled carbon nanotubes (MWCNTs) [11-15]. This could potentially increase the accruable economic revenue from pyrolysis due to the high cost of MWCNTs (> 60 USD per kg). MWCNTs possess excellent mechanical, optical, thermal and electrical properties; and have a very low mass/volume ratio that is ideal for high-tech applications such as nano-optoelectronics, flexible thin-film devices, energy storage, and structural composites [16, 17]. Waste plastic derived MWCNTs were demonstrated as a viable electrode material in oxygen reduction reaction application [18]. Conventional methods of MWCNTs synthesis use fossil sources. The conversion of the non-condensable gases to MWCNTs may provide significant

environmental benefits through the displacement of the pure carbon substrate used for the conventional MWCNTs synthesis. Synthesis of carbon nanomaterials from waste reduces the amount of solid waste and lowers the fabrication cost of the nanomaterial substantially [16].

Life cycle assessment (LCA) has great potential to drive the development of products and processes with improved environmental credentials when used at the early research stage [19]. LCA studies have reported pyrolysis of plastic waste as a better environmental option than landfill or incineration in terms of global warming potential [20, 21]. However, the environmental impacts of the synthesis of MWCNTs from non-condensable gas have not been investigated. This study provides new insights into the environmental impacts of the conversion of plastic waste into pyrolysis oil and MWCNTs. LCA facilitates the evaluation from environmental perspectives, strengthening the technology development for real world applications.

The purpose of this study was to conduct LCA of the conversion of FPPW into pyrolysis oil and MWCNTs. The objectives of this LCA were, (i) to study the environmental impacts of MWCNTs synthesis from integrated pyrolysis process, and (ii) to compare the environmental impacts of MWCNTs synthesis from two different fractions of FPPW and mixed virgin plastics. The data for the LCA were obtained from experimental findings. GaBi 6 tool with integrated 'ecoinvent' database v3.5 was used to develop the LCA model.

2. Methodology

2.1. Life cycle assessment methodology

In this study, LCA model was developed in accordance with the 'ISO 14040: Principles and Framework' and 'ISO 14044: Requirements and Guidelines' international environmental standards [22]. The goal of this LCA study was to determine the environmental impacts of pyrolysis oil and MWCNTs synthesis from FPPW pyrolysis. The

scope was to conduct a 'system' LCA covering the entire set of unit operations, which includes the products and processes. Due to the broad impact categories and the global scope of impact mechanisms, ReCiPe midpoint method was utilized for the impact assessment [23]. Hierarchist cultural perspective that represents the consensus scientific model for a 100-year timeframe was chosen for analysis according to the ISO 14044 [24-26]. Hotspot analysis was performed to depict the significant sources of emissions within the overall process, which helped to identify the areas of concern. Sensitivity analysis was conducted for various yields of MWCNTs in order to investigate the range of environmental impacts.

2.1.1. Functional unit and feedstock properties

The functional unit (FU) for the system was defined as one metric tonne of plastic. Two real FPPW mixtures were used as raw materials. The characteristics of feedstock are presented in Table S1. The main plastic components in the mixtures were polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET). Other components included nylon, aluminium, inks and adhesive. Based on the content of PET, the mixtures are denoted as PET-12 and PET-28 (PET content 11.8 and 27.5%, respectively). A model plastic mixture was used as a reference material and contained virgin plastic pellets (2 mm) from Lotte Chemical Titan Pvt. Ltd (Malaysia). The mixture was denoted as "mixed virgin plastics" (MVP) and contained PE (55 wt.%), PP (25 wt.%), polystyrene (PS, 10 wt.%) and PET (10 wt.%). The composition of MVP was selected based on the plastic distribution in municipal waste from various countries [5, 27-29]. The feedstock had moisture content less than 1 wt.%.

2.1.2. Model, assumptions and system boundary

Fig. 1 illustrates the flow diagram that represents the system boundary and incorporates the foreground process (i.e. plastic pyrolysis to MWCNTs and oil), two background processes (i.e. catalyst preparation for oil upgrading and MWCNTs synthesis), input and output flows of the studied system. In this model, the feedstock carried zero burden and started accumulating burden from the gate of the facility [30, 31]. The environmental impacts were burdened to the original plastic product, for which crude oil was recovered and processed [8]. Over 90% of the current manufactured plastics are derived from fossil energy sources [32]. Hence, all the plastics were assumed to be from fossil energy sources, and therefore biogenic carbon CO_2 offsetting was disregarded. Transportation of the plastic feedstock was excluded, as it would occur regardless whether the plastic waste is used as feed for the pyrolysis process or other existing waste management options. The system boundary begins at the waste treatment facility with the shredding of the collected FPPW. Pyrolysis and catalytic reforming for oil upgrading produced char and aluminium (i.e. solid residue in the pyrolysis reactor), spent catalyst-1 containing coke deposits, pyrolysis oil, and non-condensable pyrolysis gas. The non-condensable pyrolysis gas was utilized in the MWCNTs synthesis reactor that was loaded with catalyst-2. During the synthesis process, hydrocarbons in non-condensable pyrolysis gas were decomposed via the catalytic chemical vapor deposition (CCVD) process into MWCNTs and H_2-rich fuel gas. The MWCNTs were separated from catalyst-2 using acid washing and were subsequently dried. The wastewater from acid washing was treated with lime. The by-products of the process such as fuel gas, char and coke from catalyst-1 were combusted to flue gas and heat energy. The produced heat was utilized within the system in order to minimize burdens. Carbon, nitrogen and sulfur species were completely converted into CO_2, NO_2 and SO_2 [21]. The combustion of solid residue from pyrolysis reactor yielded aluminium (5% loss was assumed) and ash. Purge gas was assumed inessential for the large-scale continuous process, which would generate enough

pressure to ensure the continuous flow of pyrolysis gases. The conversion of FPPW to oil and MWCNTs via integrated pyrolysis-CCVD process assumed that there is a displacement effect on the production phase of the displaced product. The prevailing activities of extraction and use of original fossil source is averted due to the displacement effect. This avoids the emissions associated with the conventional production process of the products due to the proposed route [33].

2.2. Life cycle inventory

The LCA model was developed based on experimental findings. For the missing data, secondary sources such as literature, 'ecoinvent' and software database, Aspen modeling data, industrial scale systems, and commercial sources were acquired based on the best-fit principle. The mass balance data were obtained from lab-scale experiments and extended to 1 FU.

The chemicals and mass balance for background processes are presented in Table S2. Overall, 5% loss in each catalyst was assumed as the preparation of catalysts involved multiple steps. The dataset for zeolite, urea, limestone and ethanol were obtained from the 'ecoinvent' database. Due to the lack of dataset for ferric nitrate and nickel nitrate, the chemical preparation from ferric chloride and nickel sulfate were inserted into the model. The ammonium nitrate solution effluent in catalyst-1 preparation was excluded under the emissions as the material recovery step can be implemented. However, CO_2 contained in the flue gas from catalyst-1 preparation and the air emissions occurring for catalyst-2 preparation were accounted. The end-of-life scenario for catalyst-1 was excluded in the model as the catalyst can be regenerated for reuse [34]. Catalyst regeneration was confirmed during lab-scale experiments. In the LCA model, it was assumed that the catalyst can be regenerated and

reused twice. The catalyst-2 disintegrates to $NiCl_2$ and $CaCl_2$ during the acid washing process.

The product and material waste outputs obtained from the foreground processes are presented in Table 1. The CHNS elemental composition was measured using Elemental analyzer (Elementar, Germany). The recovered aluminium and pyrolysis oil displaced the 'treatment of aluminium scrap, post-consumer, prepared for recycling, at remelter' and 'diesel production, low-sulfur' datasets, respectively. Due to the lack of inventory database for MWCNTs synthesis, the data used for the MWCNTs production from acetylene were taken from Trompeta et al. [26]. The ash was sent to the inert waste sanitary landfill. The data for acid input to purify the MWCNTs and waste output are presented in the Table S3. The inventory data for hydrochloric acid and deionized water in acid washing were taken from 'ecoinvent' database. The waste output was sent to wastewater treatment plant for material recovery. Calcium oxide (78.4 kg) was added to recover Ni (74.6% as NiO and 25.4% as $Ni(OH)_2$ precipitates). The equilibrium concentration for Ni precipitation from lime addition was estimated using the Outotec HSC Chemistry Software. Calcium oxide inventory data was 'quicklime production, in pieces, loose'. Since the wastewater has relatively low $CaCl_2$ content (5.9 wt.%) and pH 5.2 and can be potentially recycled in the process, it was excluded from the system boundary.

Energy balance is presented in Table 2. Calorific values were estimated using bomb calorimeter (IKA C2000 basic, Germany). The electricity supply for the processes was custom built based on the Singapore scenario from the 2017 statistics report of Energy market authority of Singapore [35]. The production process was adopted from Japanese electricity production from natural gas 'electricity production, natural gas, combined cycle power plant' as over 95% of Singapore's electricity is from natural gas. The energy consumption data for pyrolysis process was acquired from the Zero Waste Scotland report (provided with energy

consumption breakdown information for individual sub-processes) [33] as the reported information was for industrial scale systems with comparable technology. The energy consumption data for the MWCNTs synthesis process was modelled using Aspen Plus modeling software based on the estimated gas and oil composition. In this study, the heat required for the pyrolysis and CCVD processes were supplied from the recovered heat of condensation processes generated during the pyrolysis oil recovery and fuel gas and the inherent calorific value of the plastics (HHV: 38.94 (PET-12), 29.05 (PET-28) and 39.60 (MVP) MJ kg^{-1}). The harvested heat from char, coke and fuel gas combustion was recycled back into the system to supplement the energy demand in accordance with the similar assumption made for pyrolysis of plastic waste by Fivga and Dimitriou [36].

2.3. Life cycle inventory analysis

The pyrolysis oil produced from plastics has properties similar to fossil fuels [37]. The absence of water in plastic produces pyrolysis oil fuel with high calorific value, while the absence of oxygen content renders the fuel non-acidic and non-corrosive, unlike biofuel [37-39]. Hence, pyrolysis oil can displace low sulfur diesel production [8]. A downstream distillation process can be added to the pyrolysis process if the pyrolysis oil needs to be used directly as diesel fuel or light fuel oil. Aluminium recovery can displace the re-melting process as the pyrolysis process effectively replaces the treatment process of secondary aluminium.

One of the limitations imposed in this LCA study was the absence of database for industrial MWCNTs synthesis process. In order to build the LCA model, the required data was obtained from the available literature sources. The most common MWCNTs synthesis method is the CCVD method. Trompeta et al. [26] compared the environmental impacts for the production of MWCNTs from acetylene via two routes, namely through CCVD process

over a catalyst prepared from ferric nitrate nonahydrate, and the non-catalytic process. The MWCNTs synthesis from non-condensable pyrolysis gas through CCVD is similar to the described process by Trompeta et al. with the exception of the carbon source. Based on the reported LCA results, the CCVD process accounts for one-third the environmental burden as compared to the non-catalytic process. The energy consumption for CCVD process was given to be 1,100 MJ kg^{-1} of MWCNTs. A report by Griffiths et al. [23] discussed the LCA for MWCNTs synthesis from ferrocene and toluene. 0.2 g ferrocene catalyst yielded 0.3 g MWCNTs from 8.67 g toluene. The energy consumption during the reaction period was 0.38 kWh while the heating period consumed 0.9 kWh. In this study, the method by Trompeta et al. [26] was adopted as a substitution for the MWCNTs synthesis process due to its higher yield per gram of feedstock, and lower energy consumption when compared to Griffiths et al. [23], and comparable emissions from the pyrolysis process. The catalyst and downstream recovery process were assumed the same.

2.4. Scenario description

In the first section, the environmental impacts of MWCNTs synthesis were analyzed by comparing the following two scenarios: Scenario 1 (S1), conversion of PET-12 to pyrolysis oil; Scenario 2 (S2), conversion of PET-12 to pyrolysis oil and MWCNTs. The by-products (char, coke and fuel gas) were combusted for energy recovery under both scenarios.

In the second section, the environmental impacts of various feedstock for the MWCNTs synthesis were assessed: Scenario A (S-A), conversion of PET-12 to pyrolysis oil and MWCNTs; Scenario B (S-B), conversion of PET-28 to pyrolysis oil and MWCNTs; Scenario C (S-C), conversion of MVP to pyrolysis oil and MWCNTs. The by-products (char, coke and fuel gas) were combusted under all three scenarios.

3. Results and Discussion

3.1. Environmental impacts of MWCNTs synthesis

The scenarios S1 and S2 assess the impacts of adding MWCNTs synthesis process to the existing pyrolysis plant. The S2 demonstrated beneficial effects in all the impact categories (Fig. 2). The negative numbers denote environmental benefits due to the avoided burdens through product displacement, whereas positive numbers refer to environmental burdens from direct and indirect emissions. One of the greatest benefits of S2 was obtained for the climate change potential with 242% improvement and indicated net positive effects on the environment, which was dissimilar to the negative effects associated with S1. The hotspots for the CO_2 emissions were the HCl production for acid washing process (36%), catalyst-1 (21%) and catalyst-2 (20%) preparation processes, and direct emissions from the combustion of by-products (14%), whereas the offset was significantly contributed by the MWCNTs synthesis process (76%), and pyrolysis oil (22%) (Fig. 3). Direct emissions from the catalyst preparation processes accounted for 3% (catalyst-1) and 50% (catalyst-2). The biogenic carbon contribution for climate change potential was insignificant, since most of the carbon was sourced from fossil fuels. The fossil depletion was positively influenced under both the scenarios S1 and S2, primarily due to the production of pyrolysis oil. The MWCNTs synthesis accounted for an additional 14% increase in this parameter, which stemmed from the displacement of acetylene feedstock that would have been utilized during MWCNTs synthesis.

The ionizing radiation and human toxicity (cancer) potential improvement under S2 over S1 were 248% and 30%, respectively. The impacts were principally contributed by the catalyst-1 preparation process for both the scenarios as it involves mining and extraction of zeolite and other chemicals. The pyrolysis oil offset emissions for both scenarios while the additional benefits yielded under S2 were accrued due to the MWCNTs synthesis. Minimal

differences in the environmental impacts were observed between S1 and S2 for freshwater and marine eco-toxicity. The major contributor to the positive effects on these parameters was the displacement of the treatment process of aluminium recovery, which was due to the avoidance of wastewater emissions associated with the process. The human toxicity (non-cancer) and terrestrial eco-toxicity were two of the most sensitive impact categories and recorded highest benefits for S2 when compared with S1. The major contributors for the impacts were the mining and extraction of chemicals involved in catalyst preparation processes and hydrochloric acid used for acid washing. Nickel sulfate accounted for 99% of the contribution by catalyst-2 preparation process for both the impact categories. In catalyst-1 preparation process, zeolite (60 and 52%), iron chloride (31 and 29%), and urea (8 and 18%) accounted for the human toxicity (non-cancer) and terrestrial eco-toxicity potentials, respectively. The offset was primarily contributed by MWCNTs synthesis (under S2) followed by treatment of aluminium process and pyrolysis oil yield (under S1 and S2).

Eutrophication (-0.145 Kg P eq. for freshwater and -0.014 Kg N eq. for marine) and terrestrial acidification (-2.29 Kg SO_2 eq.) potentials were negligible due to lack of any direct phosphorous emissions, insignificant nitrogen and sulfur emissions from the system. Metal depletion was largely due to the usage of metal catalysts that correspond to 2.91 Kg Cu-equivalents. Every other impact category, which are, fine particulate matter formation, freshwater consumption, land use, photochemical ozone formation, and stratospheric ozone depletion were insignificant.

The sensitivity of 1, 2.4 (original yield) and 4% MWCNTs yields were assessed. The environmental benefits increased with a commensurate increase in MWCNTs yield (Fig. 4). The inflexion point for positive effects for climate change, human toxicity (non-cancer), ionizing radiation, and terrestrial eco-toxicity potentials was ascertained when the yield of MWCNTs exceeded 2%. Significant improvement (>4%) in the MWCNTs yield was

considered essential for the minimization or removal of the human toxicity (cancer) potential. Gradual improvements in environmental benefits on fossil depletion potential (-675, -850 and -1062 Kg oil eq.) were observed for 1, 2.4 and 4% MWCNTs yields, respectively. Negligible differences in freshwater and marine eco-toxicity were observed since the impact categories were primarily dependent on the treatment of aluminium process, instead of the MWCNTs yields. Overall, the sensitivity analysis highlighted the reliance on the MWCNTs yield by the various environmental impact categories.

The pyrolysis oil (primary product) with a 68.3 wt.% yield was the major contributor in for avoiding the environmental burdens associated with fossil fuel extraction and processing. It offset most of the environmental impacts due to the process, though insufficient for certain impact categories such as climate change and human toxicity (non-cancer) potentials. The MWCNTs synthesis process played significant role in contributing to the benefits of the pyrolysis process through the conversion of non-condensable pyrolysis gas. The MWCNTs product effectively displaced the pure hydrocarbon source (i.e., acetylene) used in the conventional MWCNTs synthesis since the catalyst and downstream processing were assumed to be identical to the conventional method. The benefits reported were for the 2.4% yield of MWCNTs from the initial pyrolysis feedstock. The credit score can be further improved by increasing the MWCNTs yield as indicated in sensitivity analysis. This can be achieved either by a more efficient conversion mechanism or through recirculating the non-condensable gases. Increased MWCNTs yield would further minimize the environmental impacts due to higher carbon capture and lower flue gas emissions. Additionally, the fuel gas obtained after the MWCNTs synthesis was rich in H_2 gas with magnitudes that were 9 times higher than non-condensable gas. Although in this study it was combusted for energy recovery, the future use may focus on the H_2 fuel generation as a by-product, which would further enhance the environmental credits. Displacement effect of the aluminium product was

primarily observed when computing the eco-toxicity potentials as the model was designed to replace the treatment process instead of the aluminium as a product. The existing or alternative treatment of FPPW such as incineration would eventually recover aluminium as a product at the end of the process. Hence, in this study aluminium was disregarded as a product per se.

Despite MWCNTs substitution, human toxicity (cancer) potential indicated negative environmental impacts that interests focus for further improvements in the impact category. The use of a zeolite based catalyst is a significant contributor for this environmental impact category. Regeneration and reuse of the zeolite catalyst can minimize the environmental impacts considerably. Lopez et al. [34] reported the possibility of multiple regenerations. However, Williams and Horne [40] and Vitolo et al. [41] reported reduced effectiveness of the catalyst with multiple regenerations. Hence, the catalyst requires further enhancement and experimentation with the regeneration process which would preclude its disposal as waste. Contrastingly, alternatives for metal-zeolite catalyst may be sought to directly minimize the associated environmental impacts.

Overall, the comparison of scenario S1 with scenario S2 illustrate the environmental benefits associated with MWCNTs synthesis from non-condensable gas derived from FPPW pyrolysis. The displacement of fossil feedstock used for the conventional MWCNTs synthesis is the definitive benefit of the integrated pyrolysis process from the environmental perspective. Integration of MWCNTs synthesis can generate additional revenue stream for the existing pyrolysis plants, and provide a competitive advantage to the thermochemical process of plastic waste treatment over other recycling options.

3.2. Effect of plastic feedstock

The scenario S-A was correlated with S-B and S-C scenarios in this section (Fig. 5). To emphasize the effect of material differences, the comparison was performed for material flows, and the energy demand was excluded as it was considered constant for all scenarios. The negative environmental impact of S-B was higher in all categories when compared to the S-A, with the exception of the eco-toxicity potentials. The climate change, fossil depletion, human toxicity (cancer and non-cancer), and ionizing radiation potentials were 138, 34, 45, 14 and 73% more detrimental under S-B, respectively. The negative impacts were primarily due to lower pyrolysis oil and MWCNTs yields (Table 1) compared to S-A, and presence of 10.7% aluminium in the PET-28 feedstock that reduced the amount of plastic available for conversion. Furthermore, the direct emission of CO_2 due to the presence of high PET content contributed to the climate change potential. Contrastingly, the results of aquatic eco-toxicity (freshwater and marine) potential indicated a 190% improvement and terrestrial eco-toxicity potential indicated a 9% improvement of the environmental credits under S-B due the recovery of over 10 wt.% aluminium. The credits were due to the avoidance of wastewater emissions associated with the conventional aluminium treatment process.

The scenario S-A indicated comparable performance to S-C for most of the impact categories, with the exception of the eco-toxicity and human toxicity (non-cancer) potentials. This implied the negligible effects of impurities such as food residues, ink and adhesives present in the actual FPPW during thermal processing. However, the impurities could affect the catalyst activity and warrant further investigation. The MWCNTs yields under both scenarios were similar. The presence of 3.6% aluminium content in S-A feedstock reduces the carbon content in the plastics under treatment, and therefore affects the pyrolysis oil yield. Contrastingly, the aluminium content enhanced the credits by replacing the re-melting process for aluminium treatment that resulted in better performance of S-A in climate change, ecotoxicity and human toxicity (non-cancer) potentials as compared to S-C. Furthermore, the

comparable performance of S-C and S-A implies that the municipal plastic waste feedstock may be considered for the integrated pyrolysis treatment process to synthesize MWCNTs as the MVP feedstock represented plastic waste from different countries.

The changes in the feedstock type and composition had negligible impact on the overall thermal process. Although the quality of derived products was consistent, the yield varied corresponding to the actual plastic content. One of the worst-case scenarios such as the presence of high PET content (PET-28) lowered product yields and had larger negative environmental impacts. Consistency of product generation with the use of PET-12, PET-28, and MVP underscored the versatility of the integrated pyrolysis process in uptaking different types of municipal plastic waste. Studies by Sharma et al. [37], Anuar Sharuddin et al. [42], Miandad et al. [43], Kunwar et al. [44] and Al-Salem et al. [45] discuss the development and maturity of the technology for conversion of real plastic waste to pyrolysis oil. Overall, comparison of different feedstock indicated that using low PET FPPW was less impactful on the environment and harvested more benefits out of the system compared to high PET FPPW. The performance of FPPW and MVP were comparable for most impact categories. Additionally, the integrated pyrolysis process demonstrated its potential in treating diverse fractions of plastic waste for MWCNTs synthesis.

3.3. Limitations and future recommendations

The main limitation of the study is that the MWCNTs synthesis data were obtained from lab-scale experiments. The reported studies have multiple variants in terms of catalyst type, catalyst mass to MWCNTs yield ratio, source of carbon for MWCNTs synthesis, method of MWCNTs synthesis and others. Hence, further investigation into impacts associated with commercial MWCNTs synthesis would provide a comprehensive comparison of the associated impacts. Additionally, Haig et al. [33] reported the energy data with 60% of

the heat input wasted as heat loss. With improved design and more efficient infrastructure, this loss can be minimized. The energy data inventory is considered as the most uncertain parameter due to significant variations in the reported literature for MWCNTs synthesis. As the reported works are lab-scale studies, there could be considerable reduction in the energy demand when scaled-up to mass production as highlighted by Gavankar et al. [46].

In this study, MWCNTs were synthesized from non-condensable pyrolysis gases as an alternative to FPPW management. In order to obtain improved environmental and economic benefits, the total pyrolysis vapors (condensable and non-condensable) can be used for MWCNTs synthesis. However, the catalyst parameters need to be investigated. Moreover, the emissions associated with the integrated pyrolysis process will not be as high as the commercial systems that produce high value products such as MWCNTs using pure chemical and fossil fuel sources.

Overall, the impacts associated with the system are tolerable and the conversion of FPPW to pyrolysis oil and MWCNTs seems beneficial from environmental impact perspective. The LCA results helped to identify specific targets for future optimization of this process. The conversion of FPPW to MWCNTs renders the process circular by synthesizing materials that would have otherwise been produced from pure fossil sources. The proposed treatment process reduces the dependency on fossil fuels and facilitates in the closure of the materials loop. The treatment process provides a prospective plastic waste management option that can be classified under the circular economy concept.

4. Conclusion

The LCA study has demonstrated that integrating MWCNTs synthesis to the plastic pyrolysis process promotes significant environmental benefits in terms of climate change, ionizing radiation, fossil depletion, human toxicity (cancer and non-cancer), and terrestrial

eco-toxicity potentials. Sensitivity of different MWCNTs yields provided a range of impacts that a typical waste management facility could impart to the environment. Higher yields increased the environmental benefits commensurately, with inflexion points identified for specific potentials. In conclusion, the proposed integrated FPPW pyrolysis process helps to minimize the plastic waste that would have required disposal, improves the environmental sustainability of the pyrolysis process, increases the revenue stream of the pyrolysis process, and abnegates the use of fossil fuel sources in conventional MWCNTs synthesis process. Furthermore, the comparison of different feedstock indicated that low PET feedstock was less impactful to the environment, and harvested greater benefits out of the system when compared to high PET and presented comparable performance to MVP feedstock for most impact categories. Additionally, the integrated pyrolysis process demonstrated its potential in treating diverse fractions of plastic waste for MWCNTs synthesis. Recapture of the wasted carbon back into the product system as pyrolysis oil and MWCNTs contributes to the circularity of the pyrolysis process. The LCA model is based on multiple assumptions that add to the uncertainty of the results. Greater accuracy of the inventory data for the equipment usage and an established life cycle inventory for industrial MWCNTs synthesis would enable the LCA to be conducted with a greater degree of accuracy and representability.

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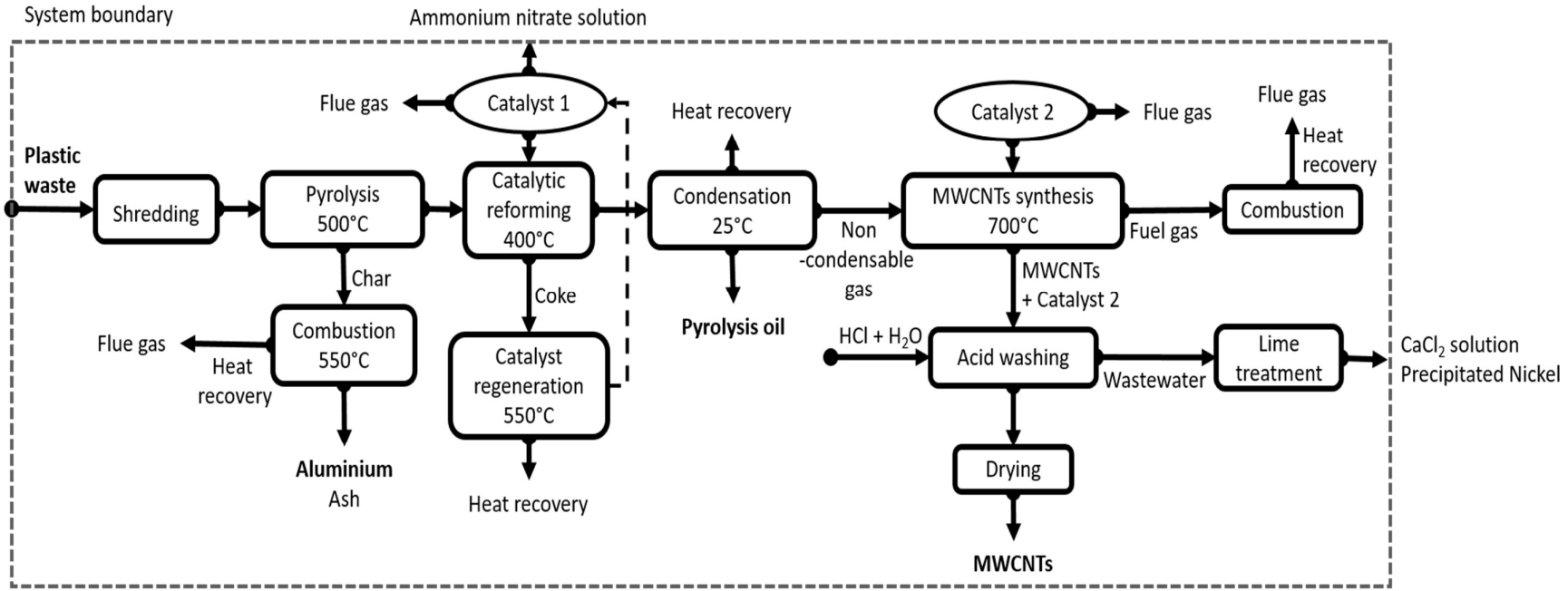

Fig. 1. The flow diagram representing the system boundary including the foreground process, background process, input and output flows of the studied system.

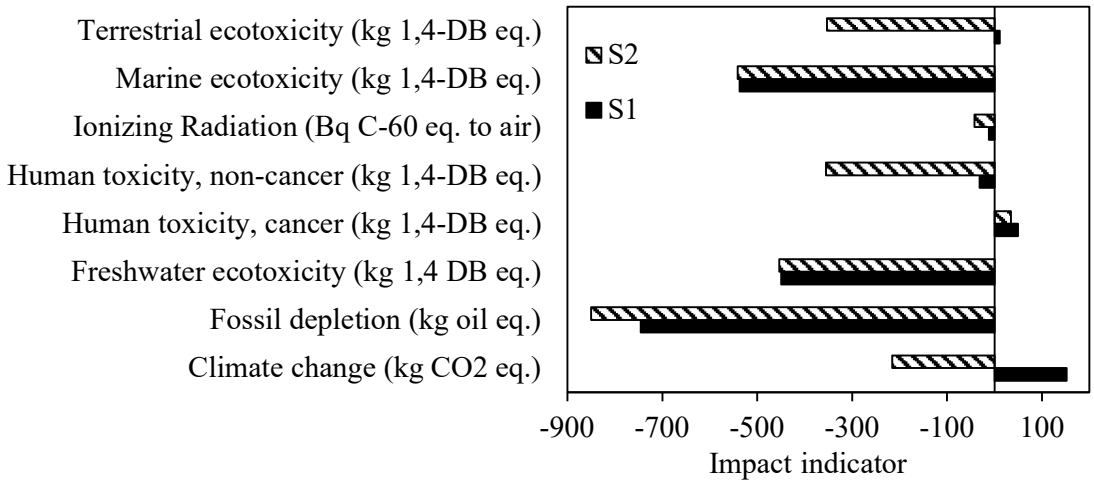

Fig. 2. The characterization results of PET-12 pyrolysis with MWCNTs synthesis (S2) presented against the PET-12 pyrolysis without MWCNTs synthesis (S1).

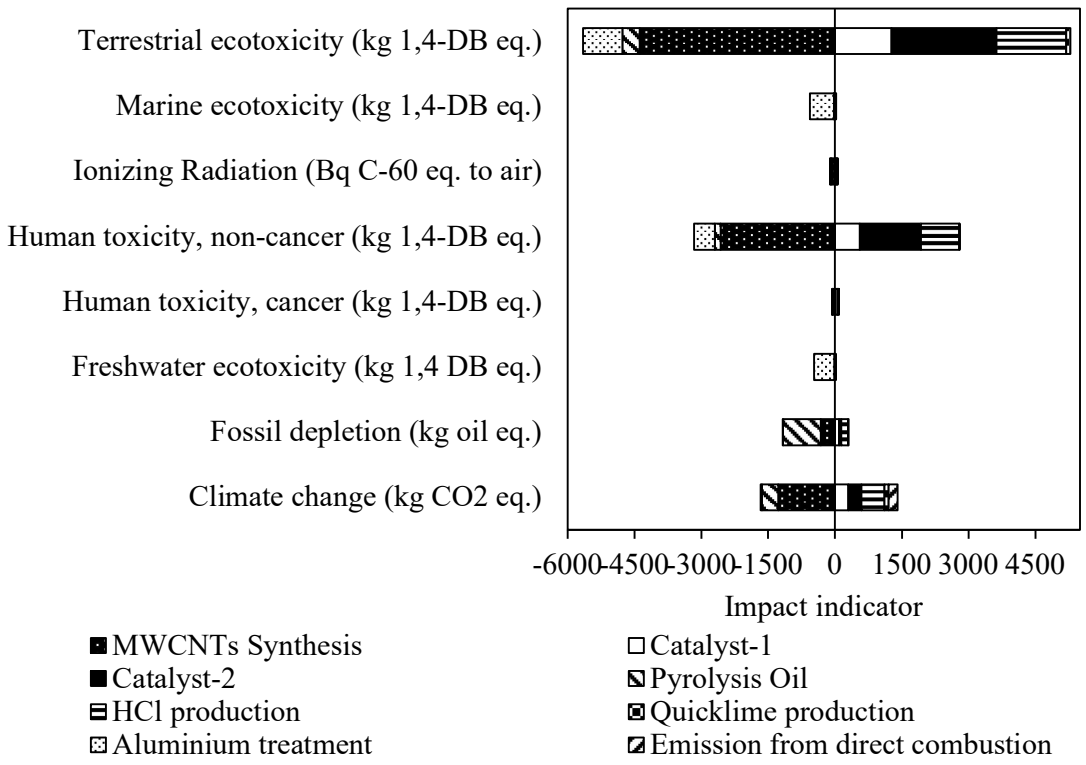

Fig. 3. Contribution of major unit operations and avoided products/processes in the system for the integrated pyrolysis process.

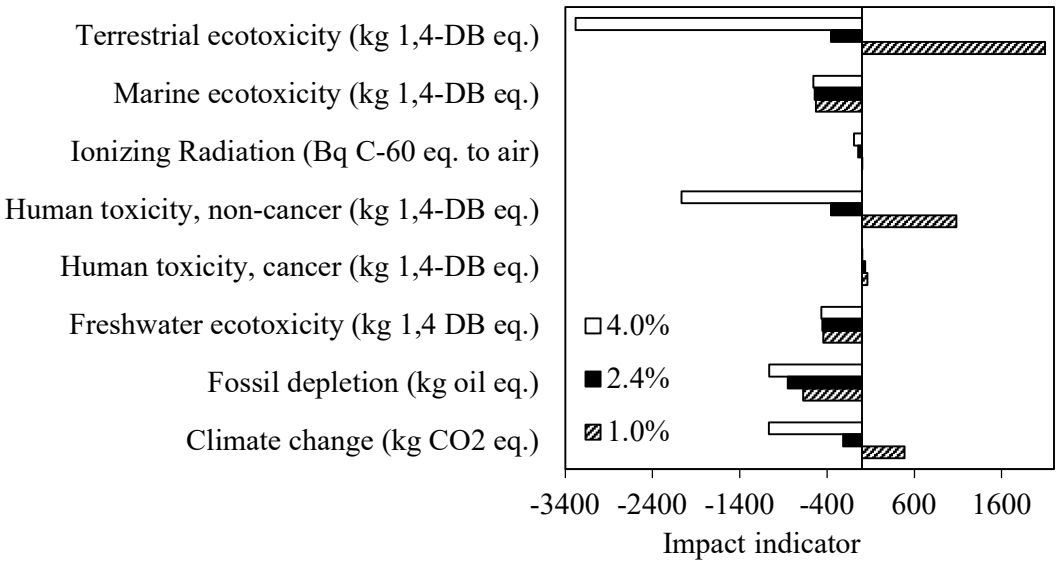

Fig. 4. Sensitivity analysis of different yields of MWCNTs from non-condensable pyrolysis gas for PET-12 feedstock.

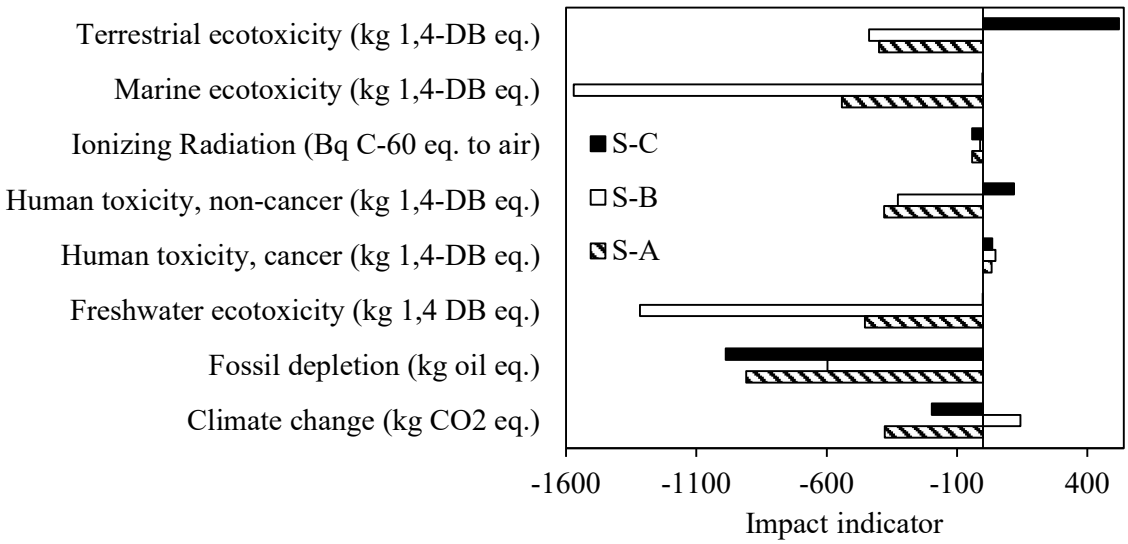

Fig. 5. Comparison of the environmental impacts of PET-12 (S-A), PET-28 (S-B) and MVP (S-C) feedstock for the integrated pyrolysis process.

Table 1. The products and material waste outputs for the foreground process.

Product/Emission	Quantity (kg FU^{-1})		
	PET-12	PET-28	MVP
MWCNTs	24.00	15.00	23.64
Pyrolysis oil	683.00	512.00	756.10
Aluminium (-5% loss)	34.77	101.65	-
Char	20.20	46.00	15.20
Flue Gas from Char			
CO_2	69.55	161.20	52.33
NO_2	1.63	1.85	1.23
SO_2	0.07	0.00	0.00
Coke	8.40	11.55	-
Flue Gas from Coke			
CO_2	27.03	38.86	-
NO_2	1.18	0.79	-
Fuel Gas	132,743 (L)	128,410 (L)	151,898 (L)
Flue Gas from Fuel Gas			
CO_2	201.04	232.32	372.16
H_2O	125.65	113.31	207.93
Ash	12.20	14.00	-

Table 2. The process energy consumed and heat value of products harvested from the system.

Process/Product	Energy input/output (MJ FU^{-1})			Source
	PET-12	PET-28	MVP	
Catalyst-1 Preparation		329.70		Estimated from industrial & commercial sources
Catalyst-2 Preparation		614.25		Estimated from industrial & commercial sources
Shredding		335.25		Estimated from industrial & commercial sources
Pyrolysis Reforming		5400.00*		Haig et al., 2013
CCVD		48235.72*		Estimated from Aspen plus software
Pyrolysis oil	26119.66	19518.75	28915.19	Laboratory analysis
Char	624.84	1418.50	470.17	Laboratory analysis
Coke	216.38	297.30	-	Laboratory analysis
Fuel Gas	3161.70	3155.39	5724.95	Laboratory analysis

*energy requirement in terms of heat