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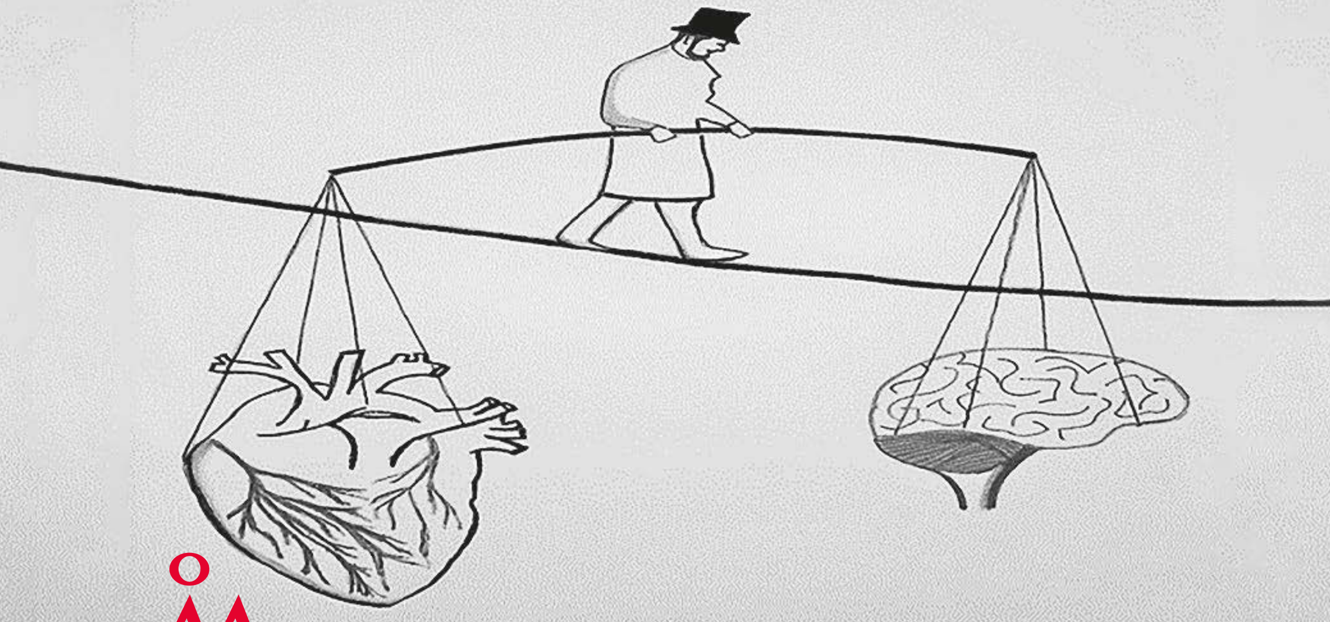
Life Cycle Assessment of Plastic Waste, its Treatment, and Application of the Upcycled Product

A Comprehensive Circular Approach



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LIFE CYCLE ASSESSMENT OF PLASTIC WASTE, ITS TREATMENT, AND APPLICATION OF THE UPCYCLED PRODUCT - A COMPREHENSIVE CIRCULAR APPROACH

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Academic Dissertation

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2021

ISBN 978-952-12-4079-9 (printed)
ISBN 978-952-12-4080-5 (digital)
Painosalama, Turku, Finland 2021

Preface

The research work presented in this thesis was primarily conducted at the Residues and Resource Reclamation Center (R3C), Nanyang Environment and Water Research Institute (NEWRI) at the Nanyang technological University as part of the on-going research projects. I thank the center director Professor Shane Snyder for his approval of this collaborative research. I acknowledge the Laboratory of Molecular Science and Engineering, Johan Gadolin Process Chemistry Centre, Department of Chemical Engineering, and thank the Rector of Åbo Akademi University for supporting my research activities and enrollment. I would like to acknowledge the travel grants for international conference participation and Abo Akademis Jubileumsfond 1968 fund for supporting the research exchange visit.

First of all, I am grateful to my Mentor, Assistant Professor Grzegorz Lisak, for providing me this opportunity to pursue the doctoral program under his supervision. Thank you for your encouragement, time, support, trust and guidance throughout these years. It has been a very productive period with scientific publications from diverse fields of research, most of which originated as a simple inquisitive idea from interesting conversations. It has been a pleasure working with you. Furthermore, I am thankful to Professor Johan Bobacka for being my supervisor and advisor. His support, involvement and feedback on my research work has helped me develop through this period. Thank you!

I acknowledge my present and former lab mates, colleagues and students who have contributed to this research work. It was indeed a great time working and learning together. I thank the reviewers of my publications and thesis for their time, positive feedbacks, and critical evaluation. I am thankful to Pramodh Vallam and BN Prakash for their support and contribution. I thank Ferose Gaffoor and Syed Ansari for their friendship, care, affection and engaging conversations about random topics. I take this opportunity to thank all my dear friends from my Biotech batch, Atti boys, Schools, Singapore, Bus route 25 and Cricket teams for the happy memories and endless laughter that we enjoyed through these years. The past will be remembered irrespective of what the future beholds for each of us. Moreover, I thank all my teachers and everyone who had been a positive influence in my life.

I am thankful to my dear parents Akbar Ali and Hayernisha for bringing me into this world. Their care, support and guidance throughout my lifetime has motivated me always. I acknowledge my siblings, relatives and in-laws for their support. More importantly, I thank my dear wife Ashrafa Jahan for her boundless love, care and affection that has strengthened me through this journey despite enduring times. I dedicate this work to my son, Mehdi Ahamed. I love you both! Finally, I am eternally grateful to The Almighty for everything, including me, my life, nature and science. فَبِأَيِّ آلَاء رَبِّكُمَا تُكَذِّبَانِ எல்லாப் புகழும் இறைவனுக்கே!

February 2021,
Singapore

Abstract

Plastic waste management is a growing global problem. Single-use flexible packaging plastic waste (FPPW) is one of the most challenging types of plastic waste to recycle due to its mixed composition (including bags, containers and films made of LDPE, HDPE, PP, PET and other materials), multi-material characteristic (multiple thin layered plastics adhered together for a single packaged product), and associated impurities (inks, adhesives and residual impurities from the packaged product). This type of plastic waste is often discarded as non-recyclable from the mechanical recycling streams. However, the use of plastics is unavoidable as the benefits outweigh other viable alternative materials in various applications. In this research, three holistic and comprehensive assessments have been conducted, including the (i) life cycle of plastic production and application, (ii) end-of-life pyrolysis treatment and upcycling to carbon nanotubes (CNTs), and (iii) application of CNTs in electrochemical sensing and end-of-life disposal of the CNTs, in order to address the FPPW management.

The specific case of the life cycle assessment (LCA) of grocery bags indicated that the environmental footprint of plastics is lower than the other prevailing alternatives, including cotton and paper, from the perspective of a metropolitan city with end-of-life incineration treatment. However, incineration of the plastic waste abnegates the circularity of material flow. Hence, a feasible and versatile integrated pyrolysis technology was developed for the FPPW treatment. The pyrolysis of plastics was evaluated using incineration ashes as a reforming catalyst in order to valorize the application of incineration ashes and to alleviate the environmental footprint associated with the utilization of synthetic catalysts. The incineration ashes demonstrated potential to be applied as a reforming catalyst in the pyrolysis of plastics to produce oil and non-condensable gas. However, further advancements in the form of pre-treatments are essential to generate performance comparable to commonly used zeolite catalysts. The LCA of the integrated pyrolysis process along with the upcycling of non-condensable gases from pyrolysis of FPPW to CNTs concluded superior environmental benefits when compared to the conventional pyrolysis of FPPW without CNTs synthesis. Notably, the integration of CNTs synthesis with the conventional pyrolysis process benefitted with diminishing the environmental footprint in terms of climate change, human toxicity, fossil depletion, ionizing radiation, and terrestrial ecotoxicity potentials. The inflexion point for the CNTs yield was identified as >2 wt.% to generate a positive effect on the environment.

Pyrolysis treatment of different waste fractions without significantly compromising the product quality highlighted the versatility of the integrated pyrolysis process. Furthermore, the synthesis of novel waste-derived CNTs (WCNTs) provides an additional revenue stream for the pyrolysis plants, enhancing their economic feasibility.

Subsequently, the synthesized WCNTs were tested in electrochemical sensing using screen-printed electrodes (SPEs) due to its enormous growth potential in diverse future applications. The electrochemical performance of WCNTs was comparable to the commercial CNTs in the detection of heavy metals, therefore, corroborating WCNTs as a viable alternative in SPEs application. The LCA determined that the WCNTs demonstrated considerable environmental advantages in comparison with the predominantly used noble metals, including gold and platinum, as electrode material. Therefore, substitution of the noble metals by WCNTs is recommended.

In conclusion, the integrated LCA approach provided context of the accrued benefits of high-value CNTs derived from plastic waste. Furthermore, the integrated LCA approach provides a measure to enhance the circularity of the material flow by identifying suitable alternatives, accentuating recycling and upcycling technologies, and determining hotspots for improvement, thereby, facilitating the environmental sustainability. The method helps to improve the recycling rates and alleviate the existing unsustainable consumption patterns. Importantly, similar LCA studies are unique and crucial to advance towards a truly circular economy and achieve the sustainable development goals.

Sammandrag

Behandling av plastavfall är ett växande globalt problem. Plastavfall bestående av flexibla engångsförpackningar (FPPW) är en av de mest utmanande typerna av plastavfall att återanvända på grund av dess blandade sammansättning (inkl. påsar, behållare och filmer av LDPE, HDPE, PP, PET och andra material), multimaterialegenskaper (flera tunna plaster sammanfogade i en enskild förpackningsprodukt) och orenheter (färger, lim och kontaminationer från den förpackade produkten). Denna typ av plastavfall avskiljs ofta som icke-återanvändbart från de mekaniska återanvändningsströmmarna. Användning av plaster är dock oundvikligt eftersom fördelarna överträffar andra möjliga alternativa material i många olika tillämpningar. I denna forskning har en holistisk, utförlig och integrerad studie genomförts inkl. livscykeln för plastproduktion, tillämpning, slutbehandling genom pyrolys, upparbetning till kolnanotuber (CNT), tillämpning av CNT i elektrokemiska sensorer, och slutförvaring av CNT, för att analysera behandlingen av FPPW.

Det specifika fallet gällande livscykelanalys (LCA) av plastkassar indikerade att det miljömässiga fotavtrycket av plast är lägre än för andra nuvarande alternativ, såsom bomull och papper, ur ett storstadsperspektiv med slutförbränning av avfall. Förbränning av plastavfall avviker dock från den cirkulära materialströmmen. Därför utvecklades en användbar, mångsidig och integrerad pyrolysteknologi för behandling av FPPW. Pyrolys av plast utvärderades genom användning av förbränningsaska som reformeringskatalysator för att uppgradera användningen av förbränningsaskor och för att minska det fotavtryck på miljön som användningen av syntetiska katalysatorer förorsakar. Förbränningsaskorna visade sig vara potentiellt användbara som en reformeringskatalysator vid pyrolys av plast för framställning av olja och icke-kondenserbara gaser. Ytterligare framsteg gällande förbehandling behövs dock för att upnå en prestanda som är jämförbar med vanligen använda zeolit-katalysatorer. En livscykelanalys (LCA) av den integrerade pyrolysprocessen tillsammans med uppgradering av icke-kondenserbara gaser från pyrolys av FPPW till CNT gav överlägsna miljöfördelar jämfört med konventionell pyrolys av FPPW utan syntes av CNT. Det var anmärkningsvärt att integreringen av CNT-syntesen med den konventionell pyrolysprocessen hade fördelen att minska det miljömässiga fotavtrycket i fråga om klimatförändring, toxicitet för människan, utarmning av fossila råvaror, joniserande strålning och ekotoxiciteten på land. Inflektionspunkten för utbytet av CNT identifierades

till >2 vikt-% för att åstadkomma en positiv effekt på miljön. Pyrolysbehandling av olika avfallsfraktioner utan att märkbart försämra produktkvaliteten underströk den integrerade pyrolysprocessens mångsidighet. Framställning av nya CNT (WCNT) utgående från avfall erbjuder dessutom en extra inkomstkälla för pyrolysanläggningen, vilket förbättrar de ekonomiska förutsättningarna.

Följande steg var att testa framställd WCNT i elektrokemiska sensorer i form av av ”screen-printade” elektroder (SPE) på grund av deras enorma tillväxtpotential inom diverse framtida tillämpningar. Den elektrokemiska prestandan hos WCNT var jämförbar med kommersiell CNT vid detektering av tungmetaller, vilket visar att WCNT är ett beaktansvärt alternativ inom SPE-tillämpninar. Livscykelanalysen (LCA) visade att WCNT hade avsevärda miljöfördelar jämfört med de mest använda ädelmetallerna, såsom guld och platina, som elektrodmaterial. Därför rekommenderas att ädelmetaller ersätts med WCNT.

Sammanfattningsvis kan nämnas att den integrerade livscykelananlysen (LCA) kunde påvisa fördelarna med värdefull CNT som framställdes från plastavfall. En integrerad LCA erbjuder ytterligare en metod för att förbättra cirkulariteten i materialströmmarna genom att identifiera lämpliga alternativ med betoning på teknologier för återanvändning och uppgradering, samt bestämning av centrala saker att förbättra, för att på så sätt gynna en miljömässig hållbarhet. Metoden hjälper till att förbättra återanvändningsgraden och att åtgärda de existerande ohållbara konsumtionssätten. Det är viktigt att notera att liknande LCA studier är unika och oumbärliga för att uppnå en verkligt cirkulär ekonomi och att uppnå hållbara utvecklingsmål.

List of publications

This thesis is based on the following publications, which are referred to in the text by their Roman numerals. The appended original publications are reprinted with permission from the publishers.

Paper I: **Ahamed, A.,** Vallam, P., Iyer, N.S., Veksha, A., Bobacka, J., Lisak, G., 2021. Life cycle assessment of plastic grocery bags and their alternatives in cities with confined waste management structure: A Singapore case study, **J. Clean. Prod.** 278, 123956.

Paper II: **Ahamed, A.,** Liang, L., Chan, W.P., Tan, P.C.K., Yip, N.T.X., Bobacka, J., Veksha, A., Yin, K., Lisak, G., 2021. In situ catalytic reforming of plastic pyrolysis vapors using MSW incineration ashes. **Environ. Pollut.** 276, 116681.

Paper III: **Ahamed, A.,** Veksha, A., Yin, K., Weerachanchai, P., Giannis, A., Lisak, G., 2020. Environmental impact assessment of converting flexible packaging plastic waste to pyrolysis oil and multi-walled carbon nanotubes. **J. Hazard. Mater.** 390, 121449.

Paper IV: **Ahamed, A.,** Ge, L., Zhao, K., Veksha, A., Bobacka, J., Lisak, G., 2021. Environmental footprint of voltammetric sensors based on screen-printed electrodes: An assessment towards "green" sensor manufacturing. **Chemosphere** 278, 130462.

Review I: **Ahamed, A.,** Veksha, A., Giannis, A., Lisak, G. Flexible packaging plastic waste – environmental implications, management solutions, and the way forward. **Curr. Opin. Chem. Eng.** 32, 100684.

Review II: **Ahamed, A.,** Liang, L., Lee, M.Y., Bobacka, J., Lisak, G., 2021. Too small to matter? Physicochemical transformation and toxicity of engineered nTiO2, nSiO2, nZnO, carbon nanotubes, and nAg. **J. Hazard. Mater.** 404, 124107.

Contribution of the author:

Papers I, III and Review I: The author conducted the experimental work, review, and the life cycle assessment modelling and analysis, prepared/drafted the manuscript, and finalized it in collaboration with the co-authors.

Papers II, IV and Review II: The author conducted the experimental and review works along with the co-authors, performed the life cycle assessment modelling and analysis, prepared/drafted the manuscript, and finalized it in collaboration with the co-authors.

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List of abbreviations

ADP-f	Abiotic depletion potential (fossil)
AP	Acidification potential
APC	Air pollution control fly ash
BET	Brunauer–Emmett–Teller
BPB	Biodegradable polymer bag
BTEX	Benzene, Toluene, Ethylbenzene, p-xylene and o-xylene
CCNT	Commercial CNT
CCNTs-SPCE	SPE modified with CCNTs
CCVD	Catalytic chemical vapor deposition
CE	Circular economy
CNT	Carbon nanotube
CtE	Counter electrode
CWB	Cotton woven bag
C-APC	Calcined air pollution control fly ash
C-ESP	Calcined electrostatic precipitator fly ash
C-IBA	Calcined incineration bottom ash
DI	Deionized
DMF	Dimethylformamide
DPASV	Differential pulse anodic stripping voltammetry
EM	Electrode material
EP	Eutrophication potential
ESP	Electrostatic precipitator fly ash
FAETP	Freshwater aquatic ecotoxicity potential
FESEM-EDS	Field emission scanning electron microscopy - energy dispersed spectroscopy
FPPW	Flexible packaging plastic waste
FU	Functional unit
GC-MS	Gas chromatography - mass spectrometry
GHG	Greenhouse gas
GWP	Global warming potential
HDPE	High-density polyethylene
HHV	Higher heating value
HPB	HDPE plastic bag
HTP	Human toxicity potential
HZSM-5	Protonated type of Zeolite Socony Mobil-5
IBA	Incineration bottom ash
ICP-MS	Inductively coupled plasma - mass spectrometry
ICP-OES	Inductively coupled plasma - optical emission spectrometry
IFA	Incineration fly ash
ISO	International organization for standardization
KPB	Kraft paper bag

LCA	Life cycle assessment
LCI	Life cycle inventory
LDPE	Low-density polyethylene
MAETP	Marine aquatic ecotoxicity potential
MSW	Municipal solid waste
MVP	Mixed virgin plastics
PE	Polyethylene
PET	Polyethylene terephthalate
PET-12	PET content 11.8%
PET-28	PET content 27.5%
PHA	Polyhydroxyalkanoate
PHBV	Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PNB	PP non-woven bag
PP	Polypropylene
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
R-APC	Raw air pollution control fly ash
R-ESP	Raw electrostatic precipitator fly ash
R-IBA	Raw incineration bottom ash
RE	Reference electrode
SM	Substrate material
SPE	Screen printed electrode
S1	Scenario 1, conversion of PET-12 to pyrolysis oil
S2	Scenario 2, conversion of PET-12 to pyrolysis oil and WCNTs
S-A	Scenario A, conversion of PET-12 to pyrolysis oil and WCNTs
S-B	Scenario B, conversion of PET-28 to pyrolysis oil and WCNTs
S-C	Scenario C, conversion of MVP to pyrolysis oil and WCNTs
TETP	Terrestrial ecotoxicity potential
tkm	tonne-kilometer
XRD	X-ray diffraction
WCNT	Waste derived CNT
WCNTs-SPCE	SPE modified with WCNTs
WE	Working electrode
ZSM	Zeolite Socony Mobil-5
15Ni-APC	15 wt.% Nickel loaded C-APC
15Ni-ZSM	15 wt.% Nickel loaded ZSM-5
30Ni-APC	30 wt.% Nickel loaded C-APC

1. Introduction

Plastic waste has become ubiquitous globally. This is attributable to the twenty-fold increase in the application of plastics in the past 5 decades. Moreover, it is predicted to double within the next 20 years [1]. The applications and types of plastic have compounded since its invention. The production of polymers (excluding fibers) has surpassed 350 million tonnes in 2018 across the world [2]. The service life of plastics extends up to 50 years, although the single-use packaging plastics are frequently utilized less than a day [3]. Polyolefins, including polyethylene (PE) and polypropylene (PP), which are produced from olefins or alkenes, are robust, lightweight, inexpensive, exceptionally ductile and malleable, and resists deterioration by air, water, cleaning solvents, and grease that the plastics encounter during the course of its service life [4-6]. The major benefit of plastics is it promotes the extension of useful life of the products (e.g., personal hygiene products and processed food). The most prevalent plastic product is PE, which represented 26% of the plastic demand across the world in 2012 [7]. PE is utilized in numerous beneficial applications, including flexible packaging bags and films that accounts for up to 65% of all the applications [8]. The surge in the utilization of plastic in diverse applications concurrently magnifies its rate of waste generation. In industrialized countries, the plastic waste contributes for a considerable proportion (30-35%) of the municipal solid waste (MSW) [9]. For example, the biggest market for plastics in the USA is packaging, which is monopolized by single-use PE and PP and contributed to 41% of the total MSW, of which 76% is landfilled, 14% is incinerated, 8% is recycled, and 2% leaks into the natural environment [10]. The plastic waste has become omnipresent, which is attributed to the upsurge of anthropocentric activities, poorly designed waste management infrastructure, indiscriminate disposal methods, inefficient and unsuitable recycling technologies, and inadequacy of public awareness [11]. However, the complete and immediate replacement of plastics is challenging as the advantages of its application exceeds those of every other viable alternative material.

One of the prevalent plastic waste streams is flexible packaging plastic waste (FPPW), which is gruelling to recycle. The recycling rate of FPPW is minimal, owing to its divergent composition, mediocre recycling value, and vestigial contaminations by the packaged product. The majority of FPPW constitutes single-use plastics, which amass at a greater scale due to its unrestrained usage. The mismanagement of MSW in low-income countries contributed to ca 66% of the macro-plastic release into the natural environment from the entire plastic value chain in 2015 [12]. Furthermore, more than 95% of the material value becomes obsolete to the economy after a brief first-use life cycle of the packaging plastic [1].

FPPW is a substantial source of marine debris and terrestrial litter that perpetually accumulates in the aquatic and terrestrial ecosystems. Polyolefins were reported as the predominant polymers recognized in the aquatic and terrestrial environments [13, 14]. The weathering effects, including oxidation at high temperatures, degradation induced by UV light, and abrasion from rocks, sand and structures made of concrete, on the macro FPPW discharged into the environment results in the formation of micro- and nano-plastics. The Caspian Sea, Persian gulf, and gulf of Oman discharged 55-158, 155-413 and 29-78 Kt of plastics from the 50 km land area within the coastline and an increase of 15, 29 and 38% is predicted by 2030, respectively [15, 16].

The discharged FPPW in natural environment (either in macro-, micro- or nano-form) interact with the indigenous fauna and flora via inhalation, ingestion, adsorption, absorption, entanglement and release of organic and inorganic pollutants. For instance, the average ingestion of micro-plastics from urban dust was reported as 353-2429 and 107-736 particles/year for adults in acute and normal exposure scenarios, respectively [17]. Fatal and sub-lethal ramifications were reported in organisms due to the ingestion and entanglement of plastics by compromising their innate competency to hunt and digest food, anti-predatory escape responses, locomotion, sense of hunger, and conceivably influence other bodily functions [18]. The nano- and micro-forms of plastics could permeate the animal and human food chains overtime promoting fatal, sub-lethal, bioaccumulation and biomagnification effects [11]. The plastic additives, including dyes, plasticizers, antioxidants, photostabilizers and retardants, and surface adsorbed chemicals could intensify the ecotoxic effect of plastics on the interacting organisms [11, 19], despite the plastics being environmentally benign and biochemically inert. For example, the plastic mulch films applied in farming presents a severe hazard to the human health and ecosystem due to the presence of endocrine disrupting phthalate esters possibly inducing developmental and reproductive toxicities, and carcinogenicity [14]. Moreover, nanoparticles were reported to be assimilated by the agricultural crops and plants [20-22]. A similar phenomenon could stimulate the bioaccumulation of nano-plastics in flora from the natural environment, subsequently leading to the human food chain. Furthermore, animal tissue and placenta samples were detected with micro-plastics [23, 24].

Apart from the reported implications, the other potential deleterious effects to the organisms include effects on metabolic processes, histopathological damage, suffocation, inflammatory/immune response, transformed enzymatic activity, altered reproductive and cellular functions, behavioural modification, hormonal disruption, genotoxicity, and cytotoxicity, all of which are deficient in knowledge. Although the threat to biodiversity by plastic litter is extensively acknowledged, the ecological consequences on ocean productivity, palatability, impact assessment models on the ecosystem damages, species dispersal, and trophic transfer in food chain remain unexplored [18, 25]. The complete detrimental effects of plastic pollution in the environment are yet to be comprehensively understood. The persistence and unexplored ramifications of plastics designate them as a concern in the natural environment. Hence, the ideal option at present is the prevention of FPPW discharge into the natural environment as avoiding the application of plastics entirely is infeasible. Furthermore, the transformation of FPPW into nano/micro-plastics would indicate a permanent and irrecoverable loss into the natural environment. Therefore, an improved waste collection and suitable treatment of FPPW is essential to avert the consequential effects of macro-, micro- and nano-plastics in the environment.

Incineration, landfilling and recycling are the existing FPPW management options. Although the FPPW is inert in a landfill or open dump, degradation and fragmentation occur due to weathering, leading to the leaching of the micro-plastics into the soil, surface and underground water streams as well as atmospheric dispersion. For example, micro-plastic concentrations of 1-25 particles/L in size ranges of 100-1000 μm were reported in landfill leachate [26]. Additionally, the FPPW could expedite the discharge of greenhouse gases (GHGs) from the deterioration of organic waste, due to the development of anaerobic conditions in a landfill. Therefore, a sanitary landfill with comprehensive GHG and leachate accumulation systems that is integrated with ensuing treatment/application is essential. Conversely, incineration averts the direct environmental contamination of the FPPW by combusting it. Nevertheless, the GHG emissions from incineration (96 Mt) of plastic waste was the greatest when compared with recycling (49 Mt) and landfill (16Mt) in 2015 [27]. This is associated with the linear mode of resource utilization where the carbon in plastics is emitted as CO_2 upon combustion.

Recycling, including mechanical, chemical and thermochemical methods, has been endorsed superior in the waste management hierarchy by the European Union [28], due to the potential improvement in the circularity of material flow. Nevertheless, the recycling is largely reliant on the practicality of selling the recovered materials to promising buyers [29]. Mechanical recycling is influenced by various factors including, the purity of the plastic materials (including the additives and ash content), the proper segregation of plastic types (including PP, high-density PE (HDPE), low-density PE (LDPE), polyethylene terephthalate (PET) and others), and the deficiency of contaminations (including food and chemical residues from the consumer product). Furthermore, the mechanical recycling method requires a series of steps including sorting/separation, cleaning and drying before re-extrusion [13, 30]. Especially, the multi-layered material fraction in the FPPW, which comprises of numerous layers of thin plastic films (including PP, PE and PET) and non-ferrous metals (including tin and aluminium), pose a considerable challenge for mechanical recycling. Therefore, a significant fraction of FPPW is rejected and discarded as non-recyclable during mechanical recycling due to its complex composition. Chemical recycling engages different chemicals to monomerize the various polymers. Vollmer et al. [31], Thiounn et al. [32] and Hong et al. [33] elaborately reviewed the various chemical recycling methods. However, the economic and industrial-scale feasibilities are uncharted as most of the research suggest that the experimental investigations are in fundamental phases of advancement with primary focus on mono-material recycling. The thermochemical recycling methods, including pyrolysis and gasification, are matured technologies with superior benefits when compared with incineration, when material and energy recovery efficiency are the paramount objectives. Pyrolysis is a thermal decomposition process in the absence of oxygen. Pyrolysis has numerous practical and environmental advantages such as reduced carbon footprint over incineration and gasification [34, 35]. It serves as a fast, efficient and complete method to treat the non-recyclable FPPW either from domestic, industrial or recovered waste streams. Hence, this research focusses on the integrated pyrolysis technology with special consideration to the pyrolysis oil upgrading and synthesis of value-added carbon nanomaterials from plastic waste, as elaborated in the following chapters. An exhaustive evaluation of the environmental aspects of the integrated pyrolysis process and product utilization is studied.

2. Pyrolysis and catalytic reforming

Pyrolysis of plastic waste is a promising technology that has been widely adopted in the recent years to address the plastic waste pollution. Pyrolysis of plastic recovers valuable energy and products including oil and non-condensable gas [34, 36]. The pyrolysis process is flexible and versatile in its capacity to treat a variety of feedstock, making it an attractive option. Besides the extraction of value-added products, the thermochemical method overcomes the barrier of multi-layered material FPPW in mechanical recycling.

The primary product of pyrolysis of plastics is volatile organic vapors, which are condensed to produce oil and non-condensable gas. The oil product is a mix of hydrocarbons consisting of olefins, aromatics, paraffins and naphthenes. Catalytic reforming is an auxiliary process to reform the pyrolysis product formation. It uses an in-line bed of catalyst through which the primary volatile organic vapors are reformed. Catalytic reforming demonstrated numerous benefits including, superior selectivity, greater yield of products, evasion of unwanted products production, and formation of oil product with low boiling point [37-39]. Textural property, acidity, pore size and pore volume of the catalysts influence the product selectivity and yield [40, 41]. The typical objective of catalytic reforming of primary pyrolysis products is to enhance the yield of BTEX compounds (i.e., benzene, toluene, ethylbenzene and xylenes) [39, 42]. BTEX compounds are valuable products with commercial interest and are representative of the pyrolytic oil quality [42-44]. Furthermore, lighter fractions of hydrocarbons, which have greater volatility, are utilized as commercial combustion fuels.

Materials of natural origin, including zeolites, silica-alumina and clay, are the chiefly used catalysts in reforming applications [45-47]. Zeolite catalysts have been extensively studied and reported to demonstrate superior degradation potential for polyolefins [43, 47]. Calcination of the catalysts is a common practice to stabilize and oxidize the precursors. Furthermore, transition metals are commonly loaded onto the base catalyst material to improve the catalytic performance [45, 48] and lower the activation energy [49]. However, periodical replacement of the catalyst is required owing to the permanent deactivation from poisoning, sintering and leaching [50], contributing to the expenses of the process and the concomitant environmental burden. Hence, the residual ashes from incineration of MSW are explored as a catalyst in **Paper II**. MSW incineration ashes frequently recognized as incineration fly and bottom ashes (IFA and IBA, respectively) are conventionally landfilled, as the end-of-life disposal option. However, exploratory research activities that intend to valorize ash usage in different utilizations, including carbon capture [51], chemical looping combustion [52], construction and land reclamation [53-55] are conducted in order to minimize the burden of waste disposal and advance circularity.

Furthermore, catalyst development is one of the prospective area of ash utilization. IBA loaded with Ni presented superior catalytic activity in the conversion of toluene to syngas [56]. The presence of high concentration of surface Ni, and basicity and greater reducibility of the IBA support were attributed to the catalytic performance. Coal, waste tire and refuse derived fuel combustion ashes used in the catalytic reforming of biomass pyrolysis vapor demonstrated considerable improvement in gas product, which was correlated to the inherent metal content of the ashes [57]. A further doping of Ni metal in the ashes resulted in ca 20% improvement in H_2 production. Similarly, 15 wt.% Ni-impregnated coal ash catalyst was used in catalytic reforming of phenol and acetic acid in the presence of steam [58]. The conversion rate of phenol and acetic acid improved from 26 and 57% to 83 and 98%, respectively, with the addition of Ni metal. In pyrolysis application of plastics, the catalytic potential of silica-alumina catalyst from coal fly ash fused with NaOH was parallel to commercial catalyst in yielding 'low boiling point' oil products during pyrolysis of LDPE [59]. Similarly, pyrolysis of waste PE using calcined coal power plant fly ash (800 °C, 5 h) reported approximately 2-times increase in the BTEX compounds when equated with thermal pyrolysis [60]. The catalytic activity was attributed to the greater silica-alumina ratio and large surface area, resulting in enhanced selectivity. These examples demonstrate the immense potential of various incineration ashes in the catalytic reforming application. However, the feasibility of MSW incineration ashes in catalytic reforming of the primary pyrolysis vapor from pyrolysis of plastics has not been investigated.

3. Upcycling of plastic waste to pyrolysis oil and carbon nanotubes (CNTs)

Collection, sorting and recycling of the plastic waste is an economically nonviable process, due to the inexpensive virgin feedstock and high volume to weight ratio of plastics that leads to heightened transportation and reprocessing costs [61]. The pyrolysis treatment processes plastic waste into oil, non-condensable gases and solid residues (**Paper III**). The pyrolysis oil can be exported as fuel, while the non-condensable gases are typically combusted for energy recovery [42, 62]. However, the economic benefit of synthesizing pyrolysis oil is inadequate. Conversely, the non-condensable gas stream was reported to be utilised in the synthesis of carbon nanomaterials, including multi-walled carbon nanotubes (CNTs) in recent studies [63-66]. Carbon nanomaterials are products of great economic value (CNTs > 60 USD/kg) that could potentially increase the revenue from pyrolysis of plastic waste. Therefore, the inferior recycling rate of plastic waste can be addressed by valorizing it into CNTs that improves the revenue stream for plant operators. The commercial demand of CNTs is increasing due to its superior mechanical, electrical, optical and thermal properties. Moreover, CNTs have a very small weight to volume ratio that renders it ideal for high-tech applications including electrochemical sensing, flexible thin-film devices, nano-optoelectronics, structural composites and energy storage [67, 68]. Additionally, the amount of solid waste requiring treatment is reduced and the fabrication cost of the nanomaterial is lowered by synthesizing CNTs from plastic waste [67], thereby improving the circularity.

Circular economy (CE) paradigm is crucial to improve the recycling rates and to address the current unsustainable consumption patterns [69]. CE helps to retain carbon in the active material flow cycle and to progress towards sustainable development by emphasizing upcycling and recycling technologies. The world economy is only 9.1% circular [70]. The major barriers to the circularity of plastics include cheap virgin feedstock, deficient infrastructure for recovery, insufficient fee for the collected waste materials, inferior properties of the recycled plastics, and lack of reliable markets for recycled materials [10]. Substantial benefits from adopting CE through a balanced approach over a 70-90 years' time horizon was suggested by a planetary model study on CE integrated with human, ecological and industrial components [69].

4. Life cycle assessment (LCA)

Life cycle assessment (LCA) is an environmental management tool to determine the global environmental impacts of production, use, recycling and disposal of goods and to compare their alternative eco-performances [6, 71]. LCA evaluates the environmental implications from a systems perspective and identifies hotspots for the improvement of environmental performance. Furthermore, LCA provides the necessary impetus for improving the environmental credentials during the development of products and processes when applied during the initial research phases [72]. The studies using LCA are progressively addressing global sustainability and environmental challenges. Pyrolysis of plastic waste has been reported as a superior environmental alternative compared to incineration or landfill by LCA studies [73, 74].

In this research, a comprehensive integrated approach has been adopted. An overview illustration of the life cycle of plastics (FPPW), end of life treatments, upcycling to CNTs, application of CNTs, and transfer to the environmental compartments and biosphere is presented in Figure 4.1. LCA strengthens the advancement of technologies for real world applications by providing an assessment from environmental perspective. To the best of my knowledge, this is the first study to investigate the environmental footprint of an integrated plastic waste value chain through LCA. The thesis provides critical insights into the pyrolytic treatment of plastic waste and highlights the environmental benefits of upcycling it to the waste management industry, and thereby, achieve greater circularity of the material flow. In **Review I,** the overall environmental implications of FPPW, possible management solutions, and future recommendations for upcycling as a circular economy concept are discussed. **Paper I** evaluates the life cycle of a commercial plastic product (plastic grocery bag) and its alternatives and identifies an environmentally friendly option from an urban city perspective. As highlighted in Chapter 1, the use of plastics is unavoidable in the modern world and hence, a feasible technology needs to be developed for treatment. **Paper II** reports the experimental findings of the catalytic reforming of plastic pyrolysis vapors using MSW incineration ashes as catalyst, in lieu of the conventional metal-zeolite catalysts. **Paper III** studies LCA of the novel pyrolysis treatment process of upcycling of FPPW to high value CNTs and oil. **Papers II** and **III** demonstrate the applicability of the pyrolysis treatment for FPPW and subsequently yield a novel product that carry significant economic and environmental advantages. **Paper IV** further validates the accrued environmental benefits of replacing the fossil derived materials with the waste-derived CNTs and also verifies the applicability of the waste-derived nanomaterial in electrochemical application. Finally, **Review II** provides the toxicity implications of the CNTs and other predominant engineered nanomaterials in the environment and biosphere.

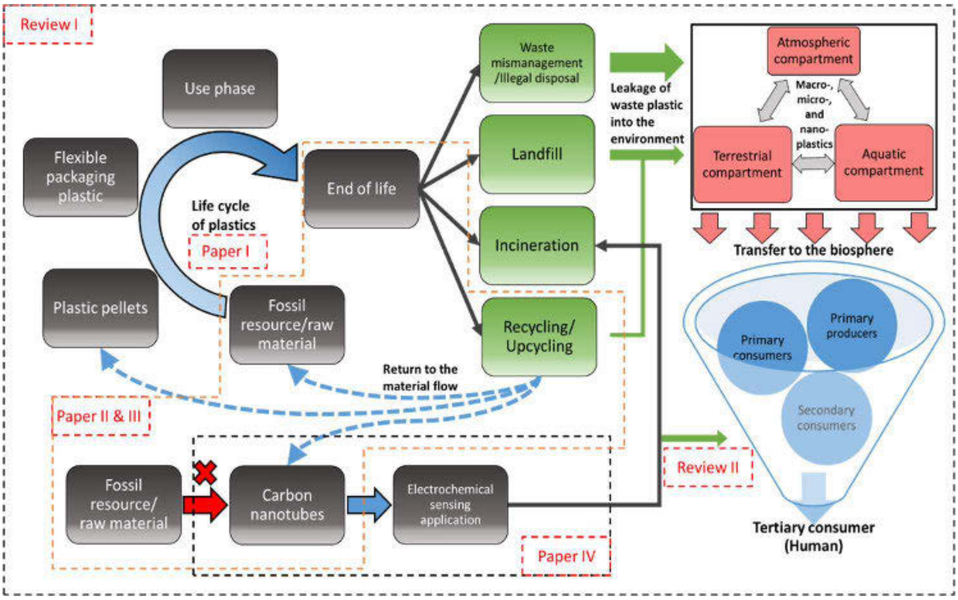


Figure 4.1. *An overview illustration of the life cycle of plastics, end of life treatments, upcycling to CNTs, application of CNTs, and transfer to the environmental compartments and biosphere*

5. Experimental and methodology

5.1. Materials

The commonly used plastic grocery bags in supermarkets and their alternatives that are accessible for public consumption were used in the LCA on grocery bags (Chapter 6.1). The standard bag (ca 31 × 53 cm; 21 μm thick; 12 L volume capacity) was made of HDPE with an average weight of 8.31 g. Although the other bags differed in capacity and dimension, the individual weight was estimated adopting 12 L capacity for each type of bag. The five types of grocery bags studied are HDPE plastic bag (HPB), cotton woven bag (CWB), kraft paper bag (KPB), PP non-woven bag (PNB), and biodegradable polymer bag (BPB).

In the pyrolysis of plastics and catalytic reforming experiments (Chapter 6.2), 2-5 mm virgin plastic pellets, including PP (70%), HDPE (24%) and LDPE (6%), procured from Lotte Chemical Titan Pvt. Ltd., Malaysia was used. Actual FPPW mixtures composing PP, PE, PET, aluminium, nylon, adhesives and inks were adopted for the LCA of pyrolysis and upcycling to CNTs and oil (Chapter 6.3). The plastic waste feedstocks were labelled as PET-12 (53.0% PE, 28.2% PP, 11.8% PET, 3.7% aluminium and others) and PET-28 (50.5% PE, 6.9% PP, 27.5% PET, 10.7% aluminium and others) referring to their respective PET contents in the mixture. Additionally, a model virgin plastic mixture (MVP) with 55% PE, 25% PP, 10% PET and 10% polystyrene (PS) was included in the LCA, as a representation of the municipal plastic waste distribution from different countries [75-78]. The moisture content of the feedstocks was <1 wt.%.

The incineration ashes used as catalysts in the pyrolysis experiments were acquired from incineration plants. The IBA residue was obtained from Senoko waste to energy incineration plant, Singapore. The IFA residues, including electrostatic precipitator fly ash (ESP) and air pollution control fly ash (APC), were procured from Tuas incineration plant, Singapore. The chemicals, including nitric acid (65% w/w), urea, nickel(II) nitrate, hexane, benzene, toluene, ethyl benzene, p-xylene and o-xylene, were procured from Sigma Aldrich. Sodium acetate, acetic acid (glacial, 100%), isopropanol and *N,N*-dimethylformamide (DMF) were purchased from Merck Pte. Ltd. High purity solvents and analytical grade reagents were utilized in all experiments and analysis. Zeolite Socony Mobil-5 (ZSM) was acquired from Alfa Aesar. Millipore Milli-Q purification system dispensed the deionized (DI) ultrapure water. Commercial CNTs (CCNTs) (95%) were purchased from Nanografi Nano Technology for electrochemical comparison with the waste-derived CNTs (WCNTs).

5.2. Plastic pyrolysis and catalytic reforming

The experimental setup of the pyrolysis of plastic and catalytic reforming is depicted in Figure 5.2.1. A stainless-steel reactor (inner diameter of 8.3 cm) contained the plastic feedstock (25 g) in a customised container and the reforming catalyst (25 g) in a steel mesh was placed on top of the container as represented in the Figure 5.2.1. The catalyst bed reformed the primary pyrolysis vapour upon heating at the desired temperature and duration (500 °C; 20 °C/min heating rate; 30 min dwelling). A thermocouple was introduced into the reactor to measure the temperature throughout the reaction duration and ensure a stable temperature profile. N_2 (99.995%, Leeden National Oxygen Ltd.) at 50 mL/min was utilized as the gas for purging the reactor system for 30 min preceding the heating, as the carrier gas to transport the pyrolysis products, and as the internal standard for quantitative assessment of the gas product. A vessel in an ice bath collected the oil product after condensation and an E-Switch gas bag accumulated the non-condensable gas product. The total mass recovery was calculated by summing up the weights of recovered oil product and feedstock residue in plastic container and the mass fraction of gas product computed using the internal standard. The catalysts used in the experiments were prepared via a series of steps, which are described in detail in Veksha et al. [79], **Papers II** and **III**. A hydraulic press was used to pelletize the dried and calcined catalysts. The pellets were subsequently crushed and screened (size: 0.2-2 mm) before application. In order to prevent the absorption of moisture, the prepared catalysts were sealed and stored at 60 °C.

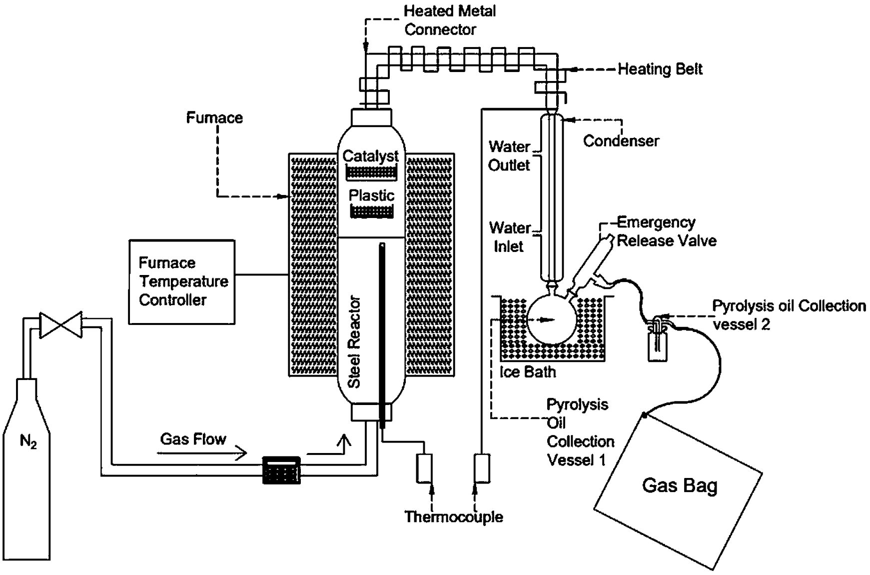


Figure 5.2.1. Laboratory system applied for the pyrolysis and catalytic reforming process of plastics

The non-condensable pyrolysis gas at 50 mL/min was fed into a vertical quartz reactor heated at 700 °C in N_2 atmosphere and contacted with the calcined Ni-Ca catalyst (size: 100-315 μm) to synthesize WCNTs. The non-condensable gas was obtained from the pyrolysis and catalytic reforming of FPPW, including PET-12 and PET-28. A detailed description of the experimental synthesis of WCNTs was reported by Veksha et al. [79] and **Paper III**. The produced WCNTs were washed with acid and water and dehydrated overnight at 105 °C.

5.3. Characterization methods

The moisture content was measured by drying the samples at 60 °C for 24 h in hot air oven. The organic fraction was calculated by combusting the dried samples at 550 °C for 2 h in a muffle furnace. CHNS elemental analyzer (Vario El Cube Elementar®) was employed to measure the elemental proportion of C, H, N and S. Bomb calorimeter (IKA C2000 basic) was used to measure the higher heating value (HHV). XRD Bruker D8 was applied to measure the X-ray diffraction (XRD) patterns of catalysts. Brunauer–Emmett–Teller (BET) method was used to determine the surface area and Barret, Joyner and Halenda method was used to calculate the average pore diameter and total pore volume of the catalysts employing Quantachrome Autosorb 1-C. Field emission scanning electron microscopy coupled with energy dispersed spectroscopy (FESEM-EDS, JEOL JSM-7600 F) was employed to characterize the morphology of the samples. In order to determine the total metal contents, microwave digestion (Milestone Ethos one) at 200 ℃ for 30 min was applied to dissolve 0.2 g of catalyst samples in 65% w/w nitric acid. The acid digested solution was filtered through a 0.45 μm PTFE syringe filter. The filtered sample was diluted with DI water and 1.2% nitric acid. Furthermore, inductively coupled plasma - mass spectrometry (ICP-MS, Thermo Scientific iCAP Q) with quantification limit = 1 μg/L and inductively coupled plasma - optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8300) with quantification limit = 1 mg/L were employed to determine the total elemental composition of the diluted samples.

The pyrolysis oil and gas products were analyzed using gas chromatography (GC). The qualitative and quantitative characterization of the oil product was conducted using GC - mass spectrometry (GC-MS, Agilent 7890B - 5977A MSD). Agilent 19091S-433 HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) was employed to separate the sample components. The carrier gas used was He, which was pumped at the flow rate of 1.2 ml/min. A detailed temperature program of the qualitative analysis with a total analysis duration of 71.25 min and quantitative analysis with a total analysis duration of 21.5 min using GC-MS is provided in **Paper II**. The qualitative analysis revealed C6-12, C13-19 and C20-35 hydrocarbon fractions representing gasoline-like, diesel-like and heavy hydrocarbons, respectively. A good linearity of the calibration curve (range 0-20 ppm; 5-point calibration) with R^2 values of 0.998, 0.995, 0.989, 0.994 and 0.995 for benzene, toluene, ethylbenzene, p- and o-xylene, respectively, were obtained for the quantification of BTEX compounds. The internal standard applied for quantifying was toluene-D8 (D 99.5%, Cambridge Isotope Laboratories, Inc). The non-condensable gas product was quantified using a GC coupled with one flame ionization detector and two thermal conductivity detectors (Agilent 7890B). He was used as the carrier gas. The gas sample collected in a gas bag was injected into the GC with front detector at 250 °C and split ratio of 80:1. The oven program was at 60 °C for 1 min initially, then raised at 20 °C/min to 80 °C, and ramped up at 30 °C/min to 190 °C, and dwelled for 1.33 min with a total analysis duration of 7 min.

5.4. LCA methodology

ISO 14040: Principles and Framework and ISO 14044: Requirements and Guidelines standards [80] with the prescribed four steps including, (1) goal and scope definition; (2) life cycle inventory (LCI); (3) life cycle impact assessment; and (4) interpretation of the results, were employed to conduct the LCA. GaBi 6 professional software tool integrated with ecoinvent v3.5 database was applied to construct the LCA models. CML 2001 method [81, 82] in Chapter 6.1 (**Paper I)** and ReCiPe midpoint method [83] in Chapters 6.3 and 6.4 (**Paper III** and **IV)** were used as the impact assessment methods, due to their global scope of impact mechanisms and broad impact categories. The consensus scientific model with hierarchist cultural perspective for a timeframe of 100 years was adopted for the analysis conforming to the ISO14044 [84-86]. In order to identify the sources of significant emission, hotspot analysis was conducted that aided in determining the contribution of individual unit operations or sub-processes within the life cycle. Furthermore, sensitivity analysis was employed to investigate the sensitivity of a specific product on the overall process. The positive values correspond to environmental burdens incurred from direct and indirect emissions, while the negative values correlate to the environmental benefits accrued from averted burdens through product displacement. The closest datasets in the ecoinvent database were applied for the respective materials wherever applicable [87]. Furthermore, specific goal, scope, functional unit (FU), system boundary model, LCI, assumptions and exclusions for each of the LCA are presented in the respective sections under Chapter 6.

6. Results and discussion

6.1. LCA of packaging plastic: the case of grocery bags – one of the major fractions of plastic waste

The LCA of single-use HDPE plastic grocery bags (HPB) and their alternatives (including 2 single-use (kraft paper (KPB) and biodegradable plastic (BPB)) and 2 reusable (PP non-woven (PNB) and cotton woven (CWB)) bags), which are currently used were compared in this chapter. The HDPE plastic grocery bags were selected as it is one of the predominantly used packaging plastic and its excessive usage highlights the extent of human carbon footprint [88]. A metropolitan city with enclosed waste management structure was adopted in the LCA model to account for the growing number of cities with dense population (>10 million inhabitants), which would further amplify the waste generation rate of plastic bags [89]. A cradle-to-grave LCA of the grocery bags, including production, transportation and end-of-life disposal via incineration was conducted. The following sections describe the life cycle modelling and results and discussion of the LCA.

6.1.1. Life cycle modelling

The goal of the LCA was to evaluate the environmental implications of HPB used for grocery shopping and equate it with the alternative options in Singapore. The scope of the LCA includes the production, transportation, waste collection, incineration and ash disposal of all grocery bag variants. The system boundary, including the foreground, background and excluded processes, is depicted in the Figure 6.1.1. The FU of the LCA was 820 million bag equivalents, which was the annual consumption of the grocery bags from supermarkets in Singapore [90]. In the case of reusable CWB and PNB, a reuse approximation wherein these bags are reused 50 times before discarding as waste was adopted equalling to 16.4 million bags for 1 FU.

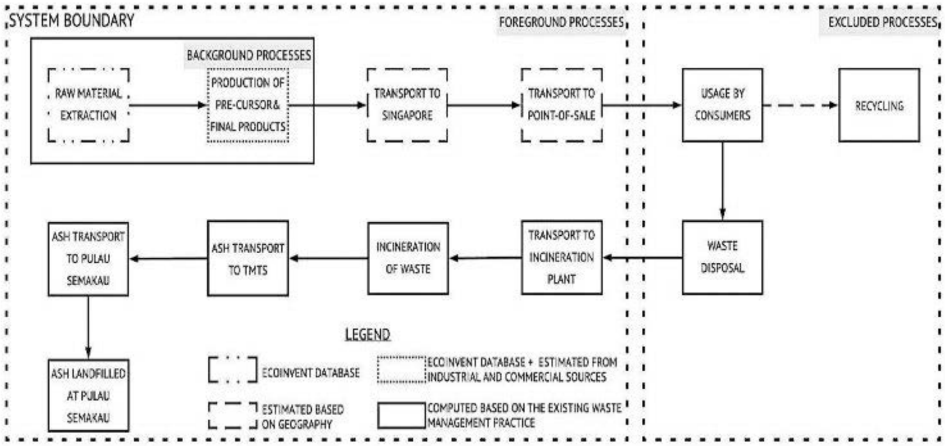


Figure 6.1.1. *The various life cycle stages of a conventional grocery bag, including foreground, background and excluded processes are depicted in the system boundary diagram. The dashed arrow imply a possible alternative recycling route for the grocery bags.*

Laboratory analysis, ecoinvent database, calculations from commercial and industrial sources, and published literature and reports were used to build the original LCI. The ecoinvent database was used for the material production, including HDPE granulates, PP granulates, cotton, kraft paper and polyester-complexed starch biopolymer. The final step of the manufacturing process of bags was modelled as reported in **Paper I**. The tonne-kilometer (tkm), a weight factor incorporated transportation distance used in LCA, for each type of bags based on 1 FU were estimated. The transoceanic transportation distances were calculated based on the material-specific import data for Singapore. The transportation distance for distribution of the bags from depot to the point-of-sale was fixed as 30 km. The generation of waste from the six zones in Singapore was allocated based on the population sizes of each zones [91], while the waste collection relies on refuse chutes inside the residential and office buildings. The collected waste was transported via trucks to the four incineration plants that was allocated based on their respective capacities and proximities. Subsequently, the ash residue generated at the incineration plants was estimated from the waste treated and the ash content of the five types of bags. The disposal of ash residue at the offshore landfill included transport by truck to the transfer station and transport by barge (30 km) to the landfill site. A detailed description of the modelling and calculations are provided in **Paper I**.

The excluded aspects from the LCA are: (i) dyes and printing inks used in the bags due to their negligible quantities and lack of data; (ii) consumer usage and storage activities due to its unquantifiable nature; (iii) transport from supermarkets to consumer destination due to the variabilities in the mode of transport and distances traversed; (iv) secondary reuse of the single-use grocery bags; (v) the mechanical device and humans employed in collection of waste and cleaning activities due to the lack of information; (vi) the transport of the vehicles after waste unloading; and (vii) transportation within the landfill. Additionally, complete combustion assumption of the bags was adopted during the incineration treatment.

6.1.2. Life cycle impact assessment results and discussion

The impact assessment results were obtained using the CML 2001 method for the five variants of the grocery bags. The 9 impact indicators, including abiotic fossil depletion potential (ADP-f), acidification potential (AP), eutrophication potential (EP), global warming potential (GWP) (excluding and including biogenic carbon), human toxicity potential (HTP), terrestrial ecotoxicity potential (TETP), freshwater- and marine- aquatic ecotoxicity potentials (FAETP and MAETP), which exemplify significant contribution to the environmental impacts are reported and discussed in detail. The other 3 impact indicators, including steady state ozone layer depletion potential, abiotic elements depletion potential and photochemical ozone creation potential resulted in insignificant implications. The material properties of the five types of bags are presented in Table 6.1.1. The LCI data for various life cycle stages of the grocery bags are presented in Table 6.1.2.

Table 6.1.1. *Material properties of the five types of grocery bags in the LCA*

	HPB	CWB	KPB	PNB	BPB
Weight (g/12L)	8.31	69.51	58.34	26.25	8.31
Bag equivalents	1	50	1	50	1
Weight equivalent of 1 FU (t)	6814	1140	47839	430	6814
Moisture content (%)	<0.1	6.2	7.0	<0.1	0.5
Organic content (%)	74.0	92.3	89.0	81.6	84.5
Ash content (%)	26.0	1.5	4.0	18.3	15.0
C (%)	61.0	44.3	41.1	71.9	74.1
H (%)	9.3	6.0	6.1	11.2	12.1
N (%)	0.1	0.4	0.1	0.1	-
S (%)	-	-	-	0.2	-
O* (%)	3.6	41.6	41.6	-	-
Calorific value (MJ/kg)	37.6	16.3	16.0	37.0	39.7

*Calculated with formula: O = 100 – (C+N+S+H) – moisture content – ash content

Table 6.1.2. *LCI developed for different grocery bags. The elemental analyzer and bomb calorimeter were used to compute the emission and energy recovery data for one FU.*

Process	Input/output flow	HPB	CWB	KPB	PNB	BPB	Respective datasets used
Grocery bag production from precursor	Power consumption for production of 1 FU (kWh)	947,376	38,303	1,597,898	126,514	947,376	SG: market for electricity, high voltage
Transport to Singapore	Transport from manufacturing source (tkm)	94,074,756	3,503,734	675,529,738	3,254,235	78,686,630	transport, freight, sea, transoceanic ship
Transport to point-of-sale	Transport, domestic distribution (tkm)	204,426	34,199	1,435,175	12,900	204,426	transport, freight, light commercial vehicle
Transport to incineration plant	Waste collection, transport (tkm)	182,777	30,577	1,283,185	11,534	182,777	municipal waste collection service by 21 metric ton lorry
Energy recovery from incineration process	Energy recovery (23%) (GJ)	58,890	4,271	176,015	3,664	62,216	SG: market for electricity, high voltage
Direct emissions	CO_2 (t)	15,244	1,850	72,129	1,136	18,507	Carbon dioxide, fossil [ecoinvent long-term to air]

from incineration of the waste	SO_2 (t)	-	-	-	2	-	Sulfur dioxide [non-urban air or from high stacks]
	NO_2 (t)	29	15	204	1	-	Nitrogen dioxide [Inorganic emissions to air]
	Ash (t)	1,771	17	1,905	79	1,020	-
Ash transport to transfer station and landfill site	Ash transport (tkm)	25,559	244	27,483	1,136	14,721	1. transport, freight, inland waterways, barge 2. transport, freight, lorry >32 metric ton

6.1.2.1. Resource extraction and production

Enormous quantities of polymers, including 52 million tonnes of HDPE and 68 million tonnes of PP were produced globally in 2015 [92]. Figure 6.1.2 illustrates the results of GWP of the five types of grocery bags. PNB demonstrated the least GWP (1.66 million kg CO_2 eq.) for the production of 1 FU, while the HPB reported a considerable footprint (13.5 million kg CO_2 eq.) due to the single-use consumption model of the fossil resource. Ethylene and propylene monomers are the raw materials in the production of HPB and PNB, respectively. Notably, the polymer production yields a superior efficiency of conversion (> 95%) from the feedstock [93]. The greatest GWP (excluding biogenic carbon) was reported for KPB. However, the KPB production demonstrated an offset of the CO_2 for GWP (including biogenic carbon) that is due to the pulpwood from trees. The benefits of the CO_2 offset are applicable when the supply of wood is determined as a renewable resource and acquired through sustainable measures by examining the growth of trees, species, and other environmental factors [94, 95]. Moreover, forest management policies, timber identification, and forest rehabilitation are some of the challenges that need to be addressed. However, the application of sustainable practices in paper production would determine the actual GWP of the KPB production. Hence, the magnitude of the GWP for KPB may vary between an offset of 43 million kg CO_2 eq. from the total to an additional 72 million kg CO_2 eq. of the overall impact. Notably, Muthu et al. [88] reported that the paper bags are predominantly produced using energy from natural gas or coal and by cutting trees, which lead to the extinction of local flora and fauna.

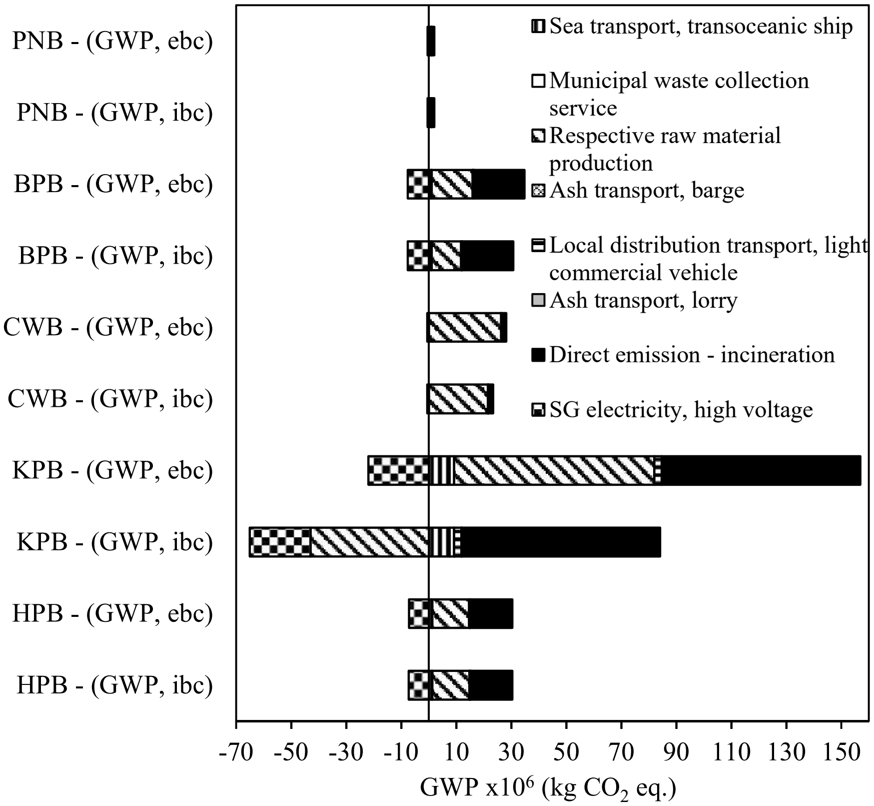


Figure 6.1.2. *Disaggregated life cycle global warming potential (GWP) of the five types of grocery bags. ebc – excluding biogenic carbon; ibc – including biogenic carbon*

Major portion of the GWP of CWB originate from the production process. A substantial consumption of fertilizers and water in the cultivation of cotton plants contribute to the various environmental implications. The cotton plants produce raw cotton, which is subsequently cleaned, baled, spun, woven into cloth, cut and stitched into cotton bags. The cotton bags are biodegradable and maintain superior tensile strength compared to HPB [96]. However, the GWP (excl. biogenic carbon) of the production process of CWB is two-fold than that of HPB and 29-times greater than PNB, despite the allocation of 50 bag equivalents for the re-usable bags. In the case of the overall GWP for 1 FU, CWB and HPB report similar results, which is predominantly contributed by the greater CO_2-eq footprint of the HPB transportation. However, the lower GWP results of re-usable bags are attainable only when there are 50 reuses, which would displace an equal carrying capacity of the single-use HPB, KPB, and BPB. The overall GWP of

HPB and BPB were similar, despite the 28% offset achieved from the embodied biogenic carbon. However, bio-plastics were reported to be more detrimental to the environment than conventional petroleum-based plastics, when traditional sources of energy, including coal, oil, and natural gas, are used in the production stages [97].

The overall life cycle impact assessment results, including all the 12 impact categories, of the five types of grocery bags are presented in Figure 6.1.3. CWB contributed to the highest FAETP and TETP and KPB resulted in the highest MAETP among the ecotoxicity potentials. The nature of conventional production process of cotton, including heavy metals discharges into freshwater and pesticide emissions into agricultural soil, are the primary causes. Similarly, a significant discharge of liquid waste is the result of paper bags production. The lowest toxicities during the production processes were reported for PNB and HPB. The greatest HTP was recorded for KPB, owing to the volatile organic carbon releases into air and heavy metals discharges into freshwater during the production of paper. The paper production was reported to cause significant impacts, including organic concentration load of wastewater [98], emission of NO_x [99], combustion of sulphur compounds [100], and discharge of chlorinated compounds [101]. Moreover, the HTP caused by transoceanic shipping of KPB was greater than the impact of the complete life cycle of PNB and HPB. Notably, a significant toxicity potential was observed for CWB in instances of re-uses fewer than 50. Similarly, PNB reported the least implications in EP and AP, while KPB caused the greatest. In comparison to HPB, BPB and CWB resulted in 1.5- and 1.7-times greater AP and 4.4- and 8.1-times greater EP, respectively. KPB constituted the highest fossil depletion potential during the production process, although the plastics are the direct product of fossil resource. The reason being the four-time greater energy requirement of paper production when compared to plastics [102]. CWB reported lower ADP-f than BPB and HPB.

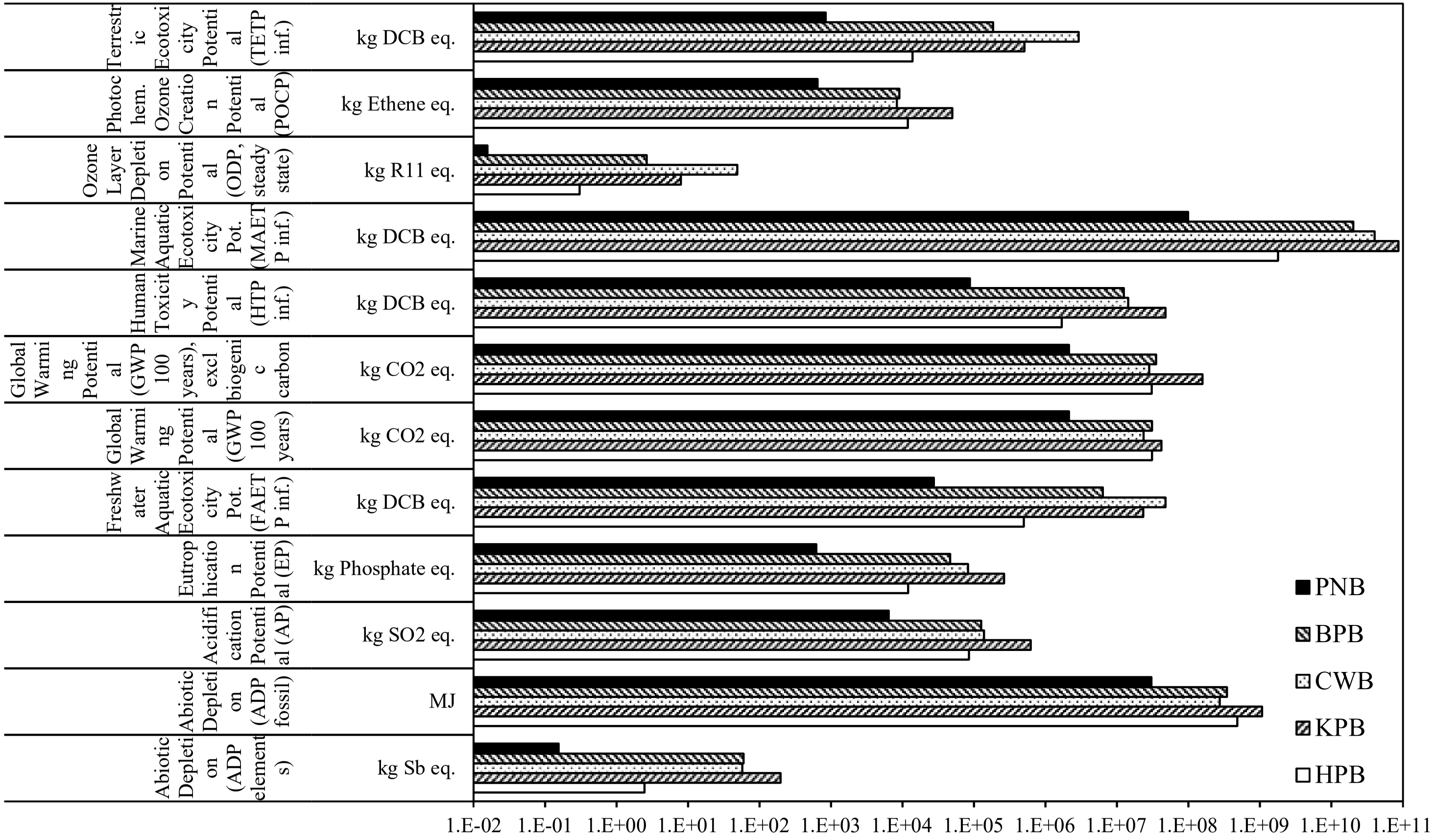


Figure 6.1.3. *The overall life cycle impact assessment results of the five types of grocery bags using CML 2001 method*

The plastic bags are light weight and provide greater carrying capacity per unit of the material than KPB and CWB. Therefore, lesser weight equivalent of plastics is required per plastic bag when compared with KPB and CWB that diminishes the overall environmental implications. Nonetheless, the magnitude of the production footprint of KPB greatly exceeds the HPB, CWB, BPB and PNB. Hence, KPB is determined to cause greater negative environmental impact on the ecosystem than other variants of grocery bags. Moreover, a linear correlation between the number of bags and impact scores were observed for re-usable bags via sensitivity analysis. For example, the impact scores of PNB doubled for 25 reuses in all the impact categories. The critical point was identified as ≥4 reuses for PNB in order to avoid emissions equal to the HPB.

6.1.2.2. Transportation

Transportation is a necessary component in the life cycle footprint of various grocery bags, given the global supply chains and dispersed locations of fossil fuel extraction and production. The inclusion of different levels of transportation involved in the supply chain and disposal is indispensable for an exhaustive LCA approach. The distances between the place of origin and the port of Singapore, local transportation to the point-of-sale, collection of waste, and disposal of ash were computed as described in the LCA model (Figure 6.1.1). The distances were converted to tkm unit based on the weight (metric tonnes) and distances (km) estimated for each variant of the grocery bag. The greatest contributor of the negative impacts was the transoceanic shipping from the place of origin, owing to the fossil fuel consumption during the long distances traversed and the tonnes of transported quantity. In the case of GWP, the overall contribution of transportation chain was 7, 5, 6 and 1% for HPB, PNB, BPB and CWB, respectively. However, the GWP (excluding biogenic carbon) for KPB generated 9% contribution from the various stages of transportation and was attributable to the heaviness of the single-use bag. The transportation involved in the domestic distribution and waste collection activities are constant. In order to reduce the GWP, the procurement of materials from nearest suppliers would commensurately reduce transport distance for shipping. Hence, the most effective impact mitigation measure would be to minimize the excessive consumption of the grocery bags and avoidance of long distance transoceanic shipping.

The KPB reported the greatest environmental impacts in all the impact categories, followed by BPB and HPB, primarily associated with the transportation of significant quantities and the single-use model. The notable contribution of the waste collection system to the ADP-f and GWP are attributable to the fossil fuel consumption and associated emissions. However, the waste collection transport reported lower environmental footprint than the local distribution transport, as higher capacity compression trucks are employed. The significant reduction in volume after combustion reduced the effects caused by ash disposal transport. A similar transport chain model can be extended to other metropolitan cities with high population density and comparable infrastructure. In cities with dispersed population, the waste collection and domestic supply chain transports would contribute to greater impacts per FU than observed in the Singapore model. Contrarily, the environmental impacts of transoceanic shipping transport might remain constant as the cities mainly import bags from prominent global producers, basing their decisions on the economic feasibility.

6.1.2.3. End-of-life and ash disposal

The most common MSW management method employed globally is incineration that yields an MSW volume reduction of up to 90% [103, 104]. The waste collected across Singapore is transported to the incineration facilities for treatment. A consequential contribution to the GWP was associated with the direct emission of CO_2 from incineration of the bags. The GWP (excluding biogenic carbon) of direct CO_2 emission accounted for 66, 7, 53, 68 and 68% for HPB, CWB, KPB, PNB and BPB, respectively. The direct emissions from incineration were uncoupled from the remaining impact categories, except EP, AP and HTP from KPB. The residual ashes from incineration process are predominantly landfilled. Although, there are certain applications explored globally including cement production, chemical looping, construction and land reclamation, and catalytic applications. The Chapter 6.2 reports the utilization of incineration ashes in the catalytic reforming of plastic pyrolysis process. In the case of HPB, a high amount of ash content was measured, possibly due to the addition of filler in bag production. The ash content can be minimized to extend the lifespan of landfills.

6.1.2.4. Air and water pollution

The influence on air and water quality varies for different types of grocery bags, due to the specific production methods, raw materials, usage of chemicals, manufacturing locations, and transportation distances, among other factors. For example, the production processes of KPB and CWB are water intensive leading to the freshwater and agricultural soil emissions. In comparison to HDPE, it was reported that paper, Mater-Bi biodegradable plastic, and cotton require over 9-, 27- and 680-times additional water per kg of fiber production, respectively [105, 106]. In metropolitan areas, the domestic supply chain transport, waste collection activities, and emissions from incineration plants are the sources of air emission, while the accompanying cleaning activities and flue gas treatment contribute to the water emissions.

Marine litter is an important aspect that can inflict significant impacts on ecological (including aquatic organisms and their coral habitats), economic (including disruption of fishing and tourism industries and expenditure on ocean clean-up activities) and social values (including environmental degradation and biomagnification leading to human health hazards) [106]. One of the most prevalent marine plastic debris is the plastic grocery bag [107-111]. Particularly, HDPE bags exhibited the greatest potential for marine littering when compared to PP, biodegradable and paper bags [106] and therefore demands a proper end-of-life treatment for plastic grocery bags to avert the discharge of waste into the natural environment. Hence, an extensive waste management practice and stringent anti-littering measures are essential in order to control the plastic pollution at source from cities in to their surrounding natural environment.

6.1.2.5. Limitations and recommendations

A common practice of the secondary use of single-use plastic bags is for garbage disposal, which could further lower the environmental footprint of HPB. This secondary application was disregarded in this study. The final ash residue for disposal was estimated based on the original ash content of the bags. However, in incineration or other thermochemical treatment plant, incomplete combustion residues would be present. The formation of the actual residue for disposal would vary depending on various factors, including material properties and temperature distribution in the furnace. The net electrical output from incineration plants ranges between 20-25% [112], which is a benefit from this product life cycle. Further improvement of the efficiency of energy recovery in incineration plants will accrue environmental benefits by offsetting the energy from conventional resources. Similarly, shifting to renewable sources of energy and improvement of the efficiency of the production process of bags would diminish the environmental footprint. The production stage was reported to consume the most energy [113] and the extrusion of plastic and printing were adjudged the most polluting in the plastic bag production process [114].

In the case of biodegradable bags, CO_2 is still released into the atmosphere upon decomposition of the material, except in instances where it is consumed by the micro- or macro-organisms (entering the biosphere) [115]. However, the CO_2 emitted from the decomposition of biodegradable bags can be excluded when biogenic material and sustainable practices are incorporated in the production process. The studies on PHBV (PHA) [116] and Mater-Bi biodegradable polymers [117] reported a degradation duration of up to 72 days under specific conditions. Similarly, only 33-36% of paper and 50-77% of cotton degraded after 45 and 90 days, respectively [118, 119]. Importantly, in the context of metropolitan cities with incineration or other thermochemical end-of-life waste treatment, the duration of biodegradation of cotton, paper, and biodegradable bags is trivial. Hence, plastics remain the preference over any of the other alternative resource- or energy-intensive options.

A ban on single-use plastic bags would incur the rise in the usage of another type of single-use bag provided the consumer behaviour remains constant [115, 120]. It would result in a greater environmental footprint than the HDPE bags, as the plastic bags demand lower energy for production among others. The imposition of plastic ban would also act a disadvantage for the consumers due to the increased costs [90]. Essentially, the productive measure is to minimize the consumption of plastic bags in order to lower the environmental implications associated with grocery bags. In the case of Singapore, more than 11 million kg CO_2 equivalent emissions can be prevented by cutting the plastic bag consumption by 50% of 2018 statistics. Additionally, secondary reuse of the single-use plastic bags, including in bin liners and as grocery shopping bags, is encouraged to minimize the environmental footprint [81, 105].

A full-scale LCA determined that HDPE plastic bags are the environmentally preferred material choice of grocery bags for the case of Singapore and similar cities (**Paper I**). Apart from grocery bags, the model can be extrapolated to other streams of plastic waste, including straws, with similar alternatives. Other thermal technologies, including pyrolysis, can be implemented to achieve greater energy recovery, carbon capture, and production of value-added materials when compared to incineration. **Chapters 6.2** and **6.3** report the technical and environmental feasibilities of the pyrolysis of plastics for the production of value-added products.

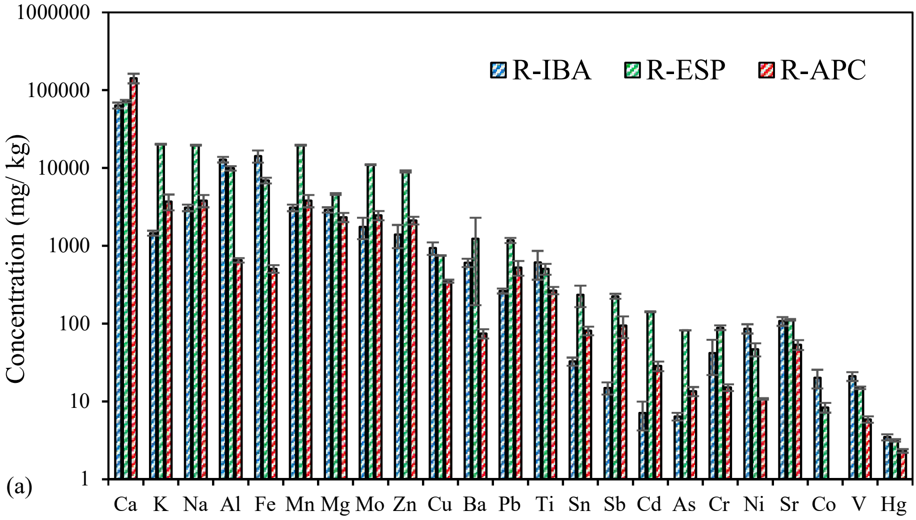
6.2. Plastic treatment via pyrolysis and catalytic reforming

As the application of plastics have been demonstrated to be the preferred option due to its comparatively smaller life cycle footprint, in this chapter, the pyrolysis treatment of plastic to synthesize pyrolysis oil and non-condensable gas products is presented. The plastic feedstock used was a mixture of HDPE, LDPE and PP that represent ca 50% of all the plastics manufactured [2], thereby constituting a considerable proportion of the FPPW stream. The MSW IFA and IBA (raw (as-received) and calcined) were tested as a promising environmental friendly and economic catalysts for the catalytic reforming application. Subsequently, Ni-loading of calcined air pollution control fly ash (C-APC) was conducted due to its desirable catalytic activity among others and benchmarked against the 15 wt.% Ni-loaded ZSM (15Ni-ZSM) catalyst. ZSM based catalysts are commonly utilized for oil reforming [47, 49, 121]. The presented results report the effect of MSW incineration ashes on the apportionment of pyrolysis oil and gaseous products.

6.2.1. Plastic pyrolysis and catalytic reforming results and discussion

6.2.1.1. Material properties of various catalysts

The diverse metal concentrations in the three raw (R-) ash samples (R-APC, R-ESP and R-IBA) are presented in Figure 6.2.1a. Ca, Na and K reported the greatest concentration in R-APC and R-ESP, while Ca, Al and Fe were abundant in R-IBA. Overall, R-ESP exhibited higher total heavy metal content than R-APC and R-IBA, with certain metals, including Cd, Sb and As, reporting concentration over 10-times higher. Other studies reported similar observations [122, 123]. The high concentration of heavy metals in R-ESP was attributed to the vaporization of metals during the incineration and subsequent adsorption and condensation on the particle surface of fly ash [124]. Conversely, the greatest Ca concentration in R-APC is correlated to the downstream addition of lime for flue gas treatment [125]. The XRD patterns of the various ashes are presented in Figure 6.2.1b. CaClOH, $CaCO_3$ and $CaSO_4$, crystalline forms were observed in R-APC and C-APC. The peak of $CaCO_3$ enhanced after calcination, while CaClOH peak diminished. The possible reason is the CO_2 reaction that converted CaClOH into $CaCO_3$ [126, 127]. In the case of R-ESP and calcined ESP (C-ESP), $K_2Ca(SO_4)_2{\cdot}H_2O$, $CaSO_4$ and NaCl crystalline phases were observed with negligible variation in the different peaks after calcination. The XRD results of R-IBA and calcined IBA (C-IBA) revealed SiO_2, $CaCO_3$ and $CaSO_4$ crystalline phases. Upon calcination, $CaCO_3$ peak diminished substantially due to the release of CO_2 from fractional decay of carbonate, while the enhanced SiO_2 peak is attributable to the transformation of amorphous to crystalline form. The ash samples are unique and innately complex from each other. Figure 6.2.1b also reported the successful imbibition of Ni in 15 wt.% Ni-loaded C-APC (15Ni-APC) catalyst. The predominance of $CaCO_3$ and NiO crystalline phases in 15Ni-APC was observed, while the CaClOH peak ceased from C-APC. Therefore, multiple distinct reactions can be attributed to the disparity in the crystalline forms observed from XRD results after calcination. Some of those reactions include, amorphous to crystalline phase transformations, potential decarbonation and carbonation reactions, removal of organic portions promoting aggregation of compounds, and chemical metamorphosis from one metallic form to another.



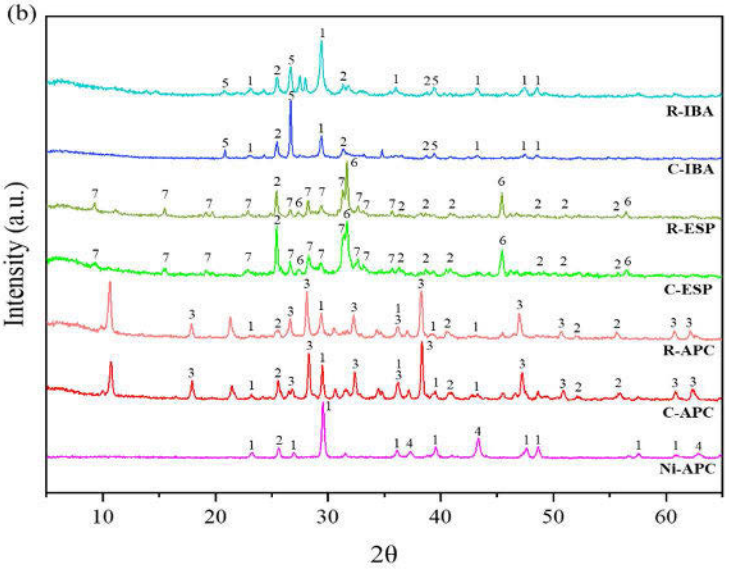


Figure 6.2.1. *Characterization results of different ash samples, including (a) Metal concentrations and (b) X-ray diffraction patterns (1 – $CaCO_3$, 2 – $CaSO_4$, 3 – CaClOH, 4 – NiO, 5 – SiO_2, 6 – NaCl and 7 – $K_2Ca(SO_4)_2 \cdot H_2O$)*

Table 6.2.1. *BET results of C-APC, 15Ni-APC and 15Ni-ZSM catalysts depicting the porous characteristics*

Catalyst	Total pore volume (cm^3/g)	Average pore diameter (nm)	BET surface area (m^2/g)
C-APC	0.003	18.3	1.5
15Ni-APC	0.018	64.7	5.6
15Ni-ZSM	0.130	16.4	267

The increase in pore volume, pore diameter, and surface area of the Ni-loaded C-APC was affirmed by BET results (Table 6.2.1). Nevertheless, 15Ni-APC exhibited inferior porous properties when compared to 15Ni-ZSM. Figure 6.2.2 presents the exterior morphology and Ni distribution from FESEM-EDS analysis of R-APC, C-APC, 15Ni-APC and 15Ni-ZSM catalysts. The APC samples exhibited inferior homogeneity with the existence of agglomerated particles, while the 15Ni-ZSM was homogenous with particle size ranging 200-500 nm. FESEM-EDS micrographs verified the uniform dispersion of Ni in 15Ni-ZSM and 15Ni-APC.

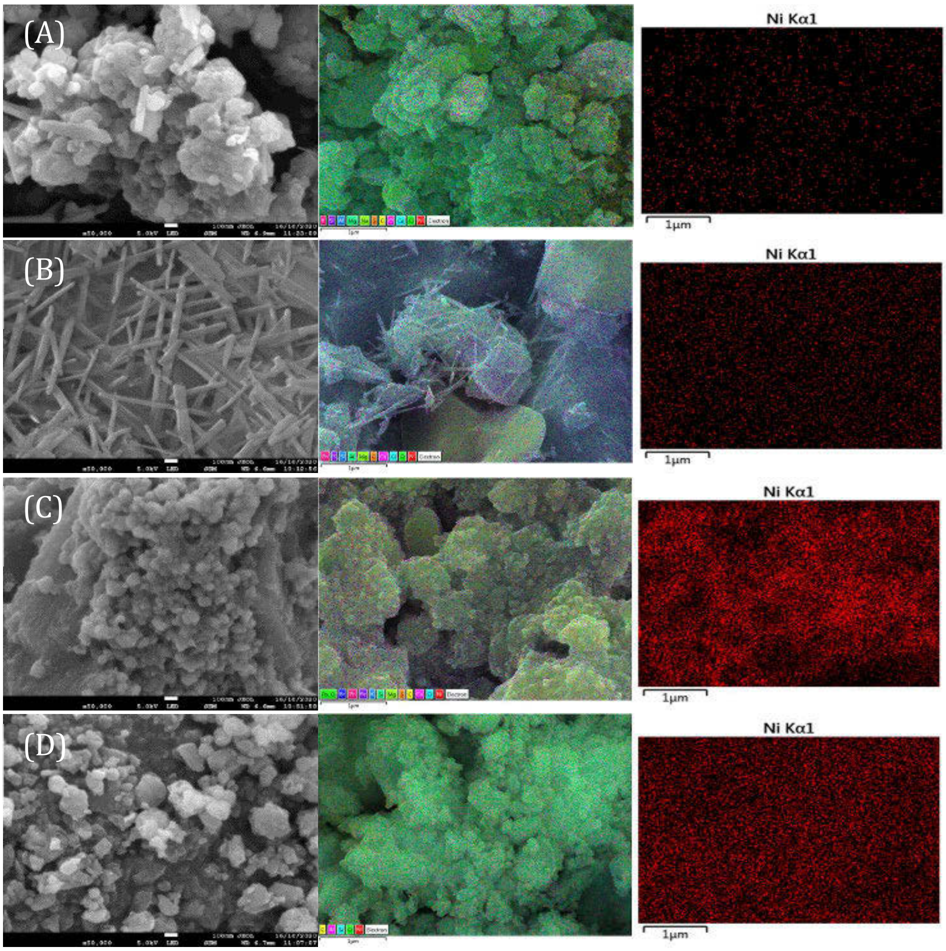


Figure 6.2.2. *The surface morphology and Ni impregnation of the (A) R-APC, (B) C-APC, (C) 15Ni-APC and (D) 15Ni-ZSM catalysts using FESEM-EDS mapping*

6.2.1.2. Pyrolysis oil product

Over 90% mass recovery was achieved for all the experiments with standard deviation of ca 6% between the triplicate experiments. The products fraction, including oil (76-82%) and gas (13-19%), yielded for all the ash samples were similar to the thermal pyrolysis (control, without catalyst), implying a minimal effect of the ash types on the product fractions. Nevertheless, incorporation of Ni metal in the C-APC catalyst produced considerably greater oil product (85-90%) and diminished the yield of gas product (4-10%), while 15Ni-ZSM reported 77% oil and 17% gas products. Similarly, clay exhibited increase in the oil fraction due to the mild acidity of the catalyst [128]. Contrarily, mesoporous arrangement with high BET surface and acidity of

15Ni-ZSM influenced the oil product formation [129-131]. The average density (0.80 ± 0.03 kg/m^3) and HHV (41.7 ± 1.2 MJ/kg) remained consistent across all oil samples.

The various fractions of hydrocarbons were determined by qualitative and quantitative characterization of the oil product. C6-12 (gasoline-like), C13-19 (diesel-like) and C20-35 (heavy hydrocarbon) compounds were categorised in the qualitative analysis [79]. The catalytic reforming using ash catalysts yielded 38-45% C6-12, 28-32% C13-19, and 23-33% C20-35 compounds, while the control experiments produced 42, 32 and 25%, respectively (Figure 6.2.3). Minor improvement in the C6-12 and C13-19 fractions were reported for the C-APC and C-IBA after calcination, however, a contrary effect was observed when using C-ESP. Conversely, the impregnation of Ni in the C-APC provided an increase in the C20-35 fraction, which was further corroborated by the results after a 30 wt.% Ni addition to C-APC (30Ni-APC) (C20-35: 40% and C6-12: 30%) as depicted in Figure 6.2.3. The phenomenon was correlated to the enlarged pore size of the Ni-loaded C-APC when compared to C-APC. Similarly, Al-MCM-41 catalysts produced greater heavy hydrocarbons when compared to HZSM-5, attributed to the inferior acidity and considerable pore size of Al-MCM-41 [43]. However, the application of 15Ni-ZSM amplified the C6-12 fraction to 67%, while declining C13-19 (19%) and C20-35 (14%) fractions.

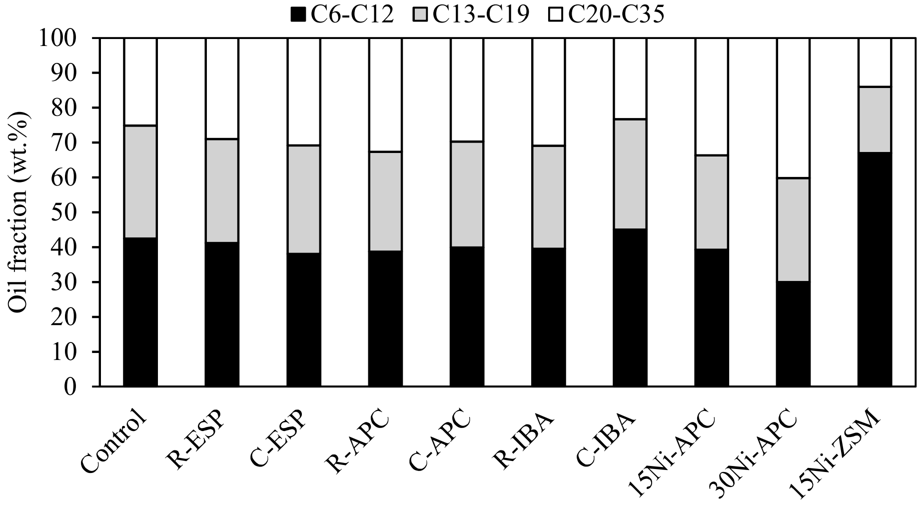


Figure 6.2.3. *Depiction of the qualitative analysis results of the three fractions of pyrolysis oil after catalytic reforming using different incineration ashes as catalysts*

Figure 6.2.4 presents the quantitative assessment results of the BTEX compounds from the pyrolysis oil after catalytic reforming using different ash catalysts. Both raw and calcined forms of IBA and APC produced greater concentrations of BTEX compounds when correlated with the control experiments. Conversely, both forms of ESP reported inferior yield of BTEX. The selective enhancement of BTEX yield ranged between 57-103% using R-APC when corresponded to the control. Furthermore, C-APC reported the greatest increase in the yield amounting to 136, 120, 102, 86 and 93% of benzene, toluene, ethylbenzene, p-xylene and o-xylene, respectively. The positive effect can be attributed to the propitious reformation of its chemical constituents upon calcination. Equivalently, pyrolysis of waste PE using calcined coal power plant fly ash yielded 1.95- to 2.03-times greater BTEX content than the thermal pyrolysis [60]. Similarly, significant increase in BTEX yield was observed for the application of R-IBA and C-IBA with the toluene production exceeded twice in magnitude using R-IBA in comparison with the control experiments. The favourable catalytic performance may be attributed to the significant Fe content in IBA [41, 132]. Although calcination diminished the BTEX yield in IBA (which is attributable to the sintering effect and crystalline phase transformations), it demonstrated a beneficial influence on the APC. The variation in the outcomes of calcination can be correlated with the innate differences of the different ash residues. The APC residues are inherently fine particles that are generated after adsorption of acidic gases from the flue gas by slaked lime and the particles trapped by bag filter. Contrarily, the IBA constitutes the residual remains of the MSW incineration. However, active components might have been exposed during the pre-processing, including milling and crushing, in R-IBA, while the subsequent calcination possibly transformed and sintered these components. Although analogous results were obtained in the qualitative assessment among the ashes, distinctive quantitative results merit the advancement of these ashes as reforming catalysts via further refining and modification.

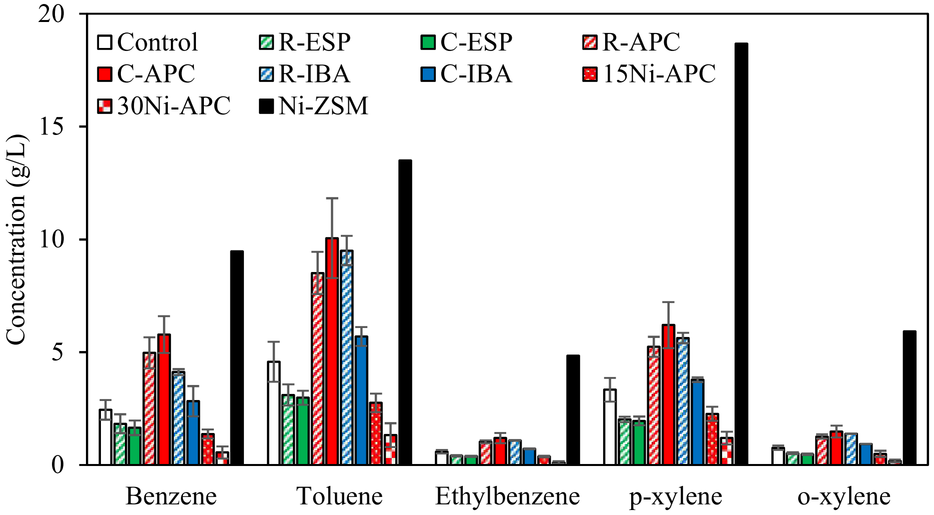


Figure 6.2.4. *Depiction of the quantitative assessment results of the BTEX compounds from the pyrolysis oil*

Additionally, the application of 15Ni-ZSM resulted in 287, 195, 721, 460 and 675% greater yield of benzene, toluene, ethylbenzene, p- and o-xylene compounds, respectively, when correlated with control experiments (Figure 6.2.4). The improvement of BTEX formation has been correlated to the metal loading of zeolites [37, 44]. The production of BTEX using Ni-APCs was inferior to the C-APC and 15Ni-ZSM, possibly owing to their larger pore size that favors heavy hydrocarbons (C20-35). Thereby, C-APC and Ni-APC exhibited substandard yield of BTEX when compared to the 15Ni-ZSM.

6.2.1.3. Non-condensable pyrolysis gas product

Figure 6.2.5 presents the various non-condensable gas products from pyrolysis of plastics when different incineration ashes are applied as reforming catalysts. Among the gas products, C3-alkenes, methane, ethane, hydrogen and C4-alkenes were the predominant compounds. The application of ash catalysts caused insignificant reformation of the gas products when compared with the control experiments, except for a minor increase in the ethane fraction yield with the application of raw catalysts. However, the Ni loaded catalysts exhibited considerable differences in the gas fractions. The 15Ni-APC and 30Ni-APC catalysts resulted in a considerable increase of ethane (230 and 305%), ethylene (42 and 86%) and methane (42 and 60%); with a concurrent reduction of C3-alkenes (35 and 100%) and C4-alkenes (33 and 69%), respectively, when compared with the control experiments. Similarly, 15Ni-ZSM exhibited an increment of ethane (223%), hydrogen

(165%) and methane (32%) and simultaneous decrease of C3-alekenes (55%) and C4-alkenes (79%), respectively, when compared with the control experiments. The effects of the Ni loaded ashes can be correlated to the catalytic conversion of the double bonded alkenes into short-chain alkanes and hydrogen. Thus, the formation of methane, ethane, ethylene and hydrogen were preferred by the metal loaded catalysts, while concurrently breaking down C4- and C3-alkenes.

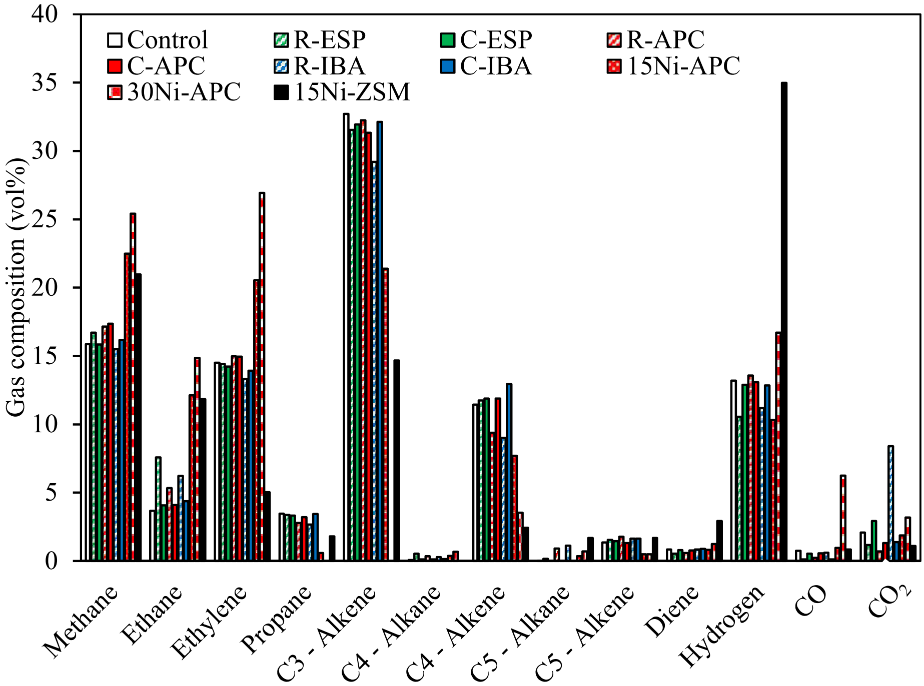


Figure 6.2.5. The composition of non-condensable pyrolysis gas product after catalytic reforming using different ash catalysts

6.2.1.4. Limitations and recommendations

APC and IBA demonstrated potential in the application of catalytic reforming of the pyrolysis vapors. One of the limitations is the requirement of post-treatment of the oil and gas products due to their inferior quality when compared to Ni-ZSM. The commercial usage of the synthesized products can be facilitated with subsequent post-treatments, including refining and distillation, of the oil and gas. For example, pyrolysis oil was blended with diesel to operate diesel engines [133, 134] and ethane and propylene were extracted from the non-condensable gas for application in the production of polyolefin [135].

Alternately, various chemical pre-treatments of the ash catalysts can be employed to improve the quality of the synthesized products. In comparison to Ni-ZSM, a greater pore diameter, mild acidity, and low surface area of the various forms of APC could engender the inferior catalytic selectivity. Further optimizing the calcination temperature after suitable pre-treatment may also augment the catalytic performance, as documented for the coal power plant fly ash by Gaurh and Pramanik [60]. Additionally, impregnation of other metal heteroatoms into the pre-treated ash structure may enhance the selective catalysis. Some studies applied Ga, Co, Ni, Zn and Fe onto the zeolite framework to improve the desired product fraction [41, 136-138].

In conclusion, the utilization of ash is appealing due to its origin from a waste resource. Although the Ni-ZSM reported considerably greater catalytic potential, incineration ash in catalytic application can be advanced to yield a comparable performance. Importantly, a potential dual benefit from the successful catalytic application of incineration ashes include offsetting the conventional catalysts used in plastic pyrolysis treatment and facilitating a possible en masse deviation of the ashes from landfill. Additionally, the change in metal leaching of the ashes before and after pyrolysis experiments was also assessed according to [139], in order to study the influence of the calcination and pyrolysis processes applied in the destabilization or stabilization of the heavy metals (**Paper II**). However, in the subsequent LCA chapter, the conventional zeolite-based catalyst was deployed for catalytic reforming due to the inferior catalytic activity of the incineration ash catalysts.

6.3. LCA of plastic waste treatment to pyrolysis oil and carbon nanotubes

In this chapter, an LCA of the pyrolysis of plastic waste to oil and non-condensable gas, and subsequent conversion of the gas to WCNTs is reported. The objectives of LCA were, (i) to investigate the environmental implications of integrated pyrolysis process, including WCNTs synthesis, and (ii) to correlate the influence of two different compositions of FPPW and MVP on the environmental implications of the WCNTs synthesis.

6.3.1. Life cycle modelling

The goal was to assess the environmental footprints of WCNTs and oil synthesis from the pyrolysis of plastic waste. The scope of the LCA includes all the unit operations involved in the system, including all the products and processes. The FU was fixed as the treatment of one metric tonne of plastic waste and the production of the associated pyrolysis oil and carbon nanotubes.

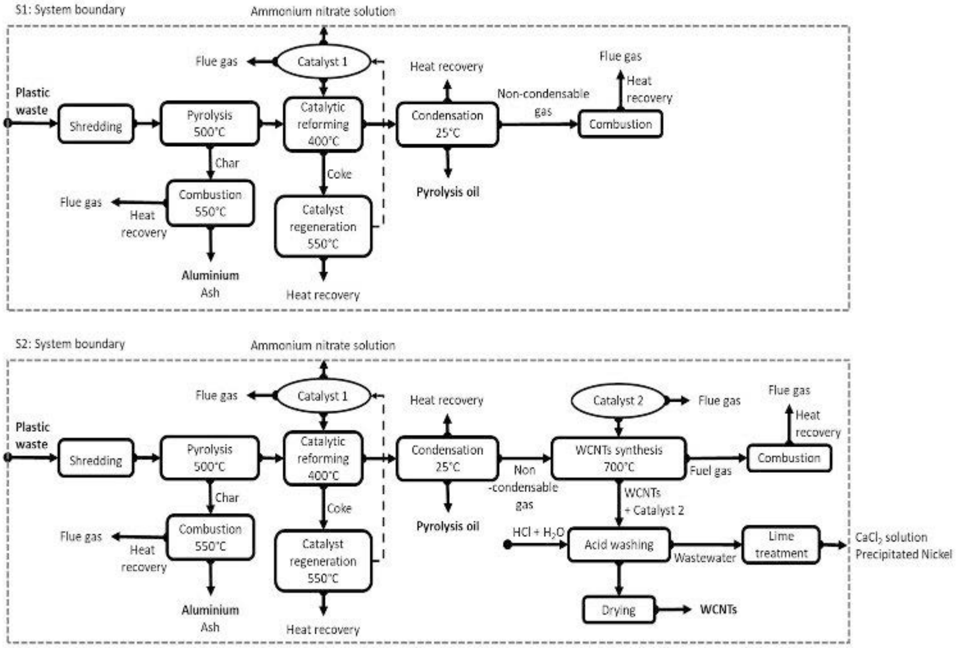


Figure 6.3.1. *The system boundary diagram, including the input and output flows and foreground and background processes of the pyrolysis treatment systems. S1: Scenario 1 (conversion of plastic waste to pyrolysis oil) and S2: Scenario 2 (conversion of plastic waste to pyrolysis oil and WCNTs).*

Figure 6.3.1 depicts the system boundary of the integrated pyrolysis process (foreground process), including the synthesis of WCNTs and oil. The system boundary comprised of two background catalyst preparation processes, the reforming catalyst (catalyst I) and catalyst applied in WCNTs synthesis (catalyst II). The FPPW feedstock was assumed to carry no burden as the environmental footprint of raw material extraction and production of virgin plastic is attributed to the original product [140-142]. The production of all the FPPW were assumed from fossil resources, as more than 90% of the existing manufacturing of plastics were reported to be from fossil resources [1]. The transportation of the FPPW to the treatment facility would ensue irrespective of the waste management method, hence, was excluded. However, a detailed transportation model was included in the LCA of plastic grocery bags (Chapter 6.1). According to the LCA model, the as-received FPPW is shredded, followed by pyrolysis and catalytic reforming. Pyrolysis oil, non-condensable pyrolysis gas, solid residue (comprising char, aluminium and ash), and spent catalyst I were obtained after the pyrolysis and catalytic reforming process. Subsequently, WCNTs and fuel gas were synthesized from the decomposition of non-condensable pyrolysis gas contacted with catalyst II via catalytic chemical vapour deposition (CCVD) process. The synthesized WCNTs were extracted from catalyst II by washing with acid and DI water and dried in a hot air oven. Lime treatment was applied for the wastewater generated after the acid washing of synthesized CNTs. The energy burden of the system was alleviated by recovering heat energy from the combustion of by-products including char residue, fuel gas, and coke deposited from catalyst I. Complete combustion of C, S and N was assumed for the heat recovery process emitting CO_2, SO_2 and NO_2 [74]. Ash and aluminium (a loss of 5% was assumed during treatment and recovery) were obtained from the combustion of solid residue. Purge gas was excluded as the industrial-scale pyrolysis process would achieve continuous flow of the pyrolysis gases due to the creation of positive pressure in the reactor system. The application of system expansion method averts the emissions affiliated with the conventional products [143].

The primary source of LCI was the experimental findings. However, secondary sources including, ecoinvent database, literature, data from Aspen modelling and HSC software simulation, published information for industrial-scale systems, and specification data for commercial equipment were adopted for the missing information. The results from the laboratory-scale experiments were extended for 1 FU. A detailed information on the chemicals used and material balance in the background processes is provided in **Paper**

III. A mass loss of 5% was assumed for each catalyst due to the numerous steps involved in the preparation process. Limestone, ethanol, HCl, zeolite, nickel sulphate, ferric chloride, quicklime, DI water and urea datasets were extracted from the ecoinvent database. The catalyst preparation from nickel sulphate and ferric chloride were adopted due to the lack of datasets for nickel and ferric nitrates. Due to the possible implementation of a material recovery step, the waste effluent which comprised of ammonium nitrate solution during catalyst I preparation process was disregarded from the system boundary. Nevertheless, air emissions from catalyst I and II preparation processes were incorporated. Due to the possible reuse of catalyst I, the end-of-life of catalyst I was excluded [144]. Laboratory experiments confirmed the feasibility of the catalyst I being regenerated and reused, hence, two applications of the catalyst was assumed in the LCA model. However, the acid washing process employed for the recovery of WCNTs disintegrates the catalyst II into $CaCl_2$ and $NiCl_2$.

The output flow data, including product yield and emission for flue gas, are presented in Table 6.3.1. The pyrolysis oil displaced 'diesel production, low sulfur' [140]. The oil product from pyrolysis of plastics was reported to demonstrate comparable characteristics to the fossil fuels [145]. Furthermore, oil product with high HHV, non-corrosive and non-acidic nature is formed from pyrolysis of plastics due to its negligible water content and low oxygen content when compared to biofuel [145-147]. The aluminium recovered from combustion of char displaced 'treatment of aluminium scrap, post-consumer, prepared for recycling, at remelter', since the aluminium metal product would be recovered via any of the alternate thermal treatment processes. The unavailability of data for the industrial-scale CNTs synthesis is one of the limitations in this LCA model. CCVD is the predominant CNTs synthesis method. The environmental footprint comparison of the synthesis of CNTs using a non-catalytic and CCVD process from acetylene feedstock was conducted by Trompeta et al. [86]. The non-catalytic process reported thrice the environmental footprint than the CCVD process. The CCVD process applied by Trompeta et al. [86] is analogous to the WCNTs synthesis from non-condensable gas and hence, adopted in this LCA. Identical downstream material recovery process and catalyst utilization were assumed. The chemical consumption data for WCNTs purification and the respective waste emissions are provided in detail in **Paper III**. The liquid waste was treated at the wastewater treatment plant with material recovery. The LCA model included Ni (25.4% as $Ni(OH)_2$ and 74.6% as NiO precipitates) recovery with the addition of 78.4 kg CaO, which was estimated by deriving the equilibrium concentration for Ni precipitation using Outotec HSC Chemistry Software. The remaining wastewater was excluded from the system boundary due to the low $CaCl_2$ concentration (5.9 wt.%; pH 5.2) that can be conceivably recycled.

Table 6.3.1. *Chart depicting the products and waste emission of the integrated pyrolysis process*

Product/Emission	Quantity (kg/FU)		
	PET-12	PET-28	MVP
WCNTs	24.00	15.00	23.64
Pyrolysis oil	683.00	512.00	756.10
Aluminium (−5%)	34.77	101.65	-
Char residue	20.20	46.00	15.20
Flue gas from char residue			
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	-

The data for energy input and output is provided in Table 6.3.2. The electricity inventory was customized according to the report of the Energy Market Authority of Singapore [148]. The dataset applied was ‘electricity production, natural gas, combined cycle power plant’ acquired from the Japanese data repository in ecoinvent database. The data for energy consumption during industrial-scale pyrolysis and catalytic reforming of plastics was adopted from Haig et al. [143]. Aspen plus software program was utilized to model the energy consumption involved in WCTNs synthesis from non-condensable pyrolysis gas. The innate heating value of plastics (HHV (MJ/kg): 38.9 for PET-12; 29.1 for PET-28; and 39.6 for MVP), the reclaimed heat of condensation of pyrolysis oil, the recovered heat from the combustion of coke, char and fuel gas were directed to supplement the heat energy needed for the pyrolysis and CCVD processes. A similar assumption was adopted by Fivga and Dimitriou [149] for the pyrolysis of plastic waste.

Table 6.3.2. *The input and output energy flow values of the integrated pyrolysis system*

Process /Product	Energy input/output (MJ/FU) PET-12	PET-28	MVP	Source
Shredding	335.25			Computed from commercial & industrial sources
Catalyst-1 Preparation	329.70			Computed from commercial & industrial sources
Catalyst-2 Preparation	614.25			Computed from commercial & industrial sources
Pyrolysis and Reforming	5400.00*			Adopted from Haig et al. [143]
CCVD	48235.72*			Calculated using Aspen plus software
Pyrolysis oil	26119.66	19518.75	28915.19	Derived from laboratory analysis
Fuel Gas	3161.70	3155.39	5724.95	Derived from laboratory analysis
Char	624.84	1418.50	470.17	Derived from laboratory analysis
Coke	216.38	297.30	-	Derived from laboratory analysis

*energy requirement in terms of heat

6.3.2. Life cycle impact assessment results and discussion

6.3.2.1. Environmental impacts of WCNTs synthesis

The following two scenarios, Scenario 1 (S1): conversion of PET-12 to pyrolysis oil and Scenario 2 (S2): conversion of PET-12 to pyrolysis oil and WCNTs were assessed and the environmental impacts are discussed in detail subsequently. The environmental implications of including a WCNTs synthesis process from non-condensable pyrolysis gas are highlighted via comparison of S1 and S2. As depicted in Figure 6.3.2, S2 presented positive effects in all the impact categories. Notably, the climate change potential reported a 2.4-times enhancement causing an ameliorative effect on the environment, unlike in the case of S1. The production footprint of HCl applied in acid washing (36%), the preparation processes of catalyst I (21%) and catalyst II (20%), and direct emissions originating from the combustion of by-products, including coke, char and fuel gas, for energy recovery (14%) were identified as the primary sources of CO_2 emissions. The WCNTs (76%) and pyrolysis oil (22%) production were the predominant products contributing to the beneficial effects (Figure 6.3.3). It highlights the environmental benefit of adding a WCNTs process to an existing pyrolysis plant. From the catalyst preparation processes, the direct emissions accounted for 50% in catalyst II and 3% in catalyst I. The CO_2 offsetting due to the biogenic carbon resource was negligible due to the production of plastics from fossil resources. The production of pyrolysis oil contributed positively to the fossil depletion potential in both S1 and S2. However, an additional 14% improvement was observed with the inclusion of WCNTs synthesis, due to the substitution of acetylene feedstock.

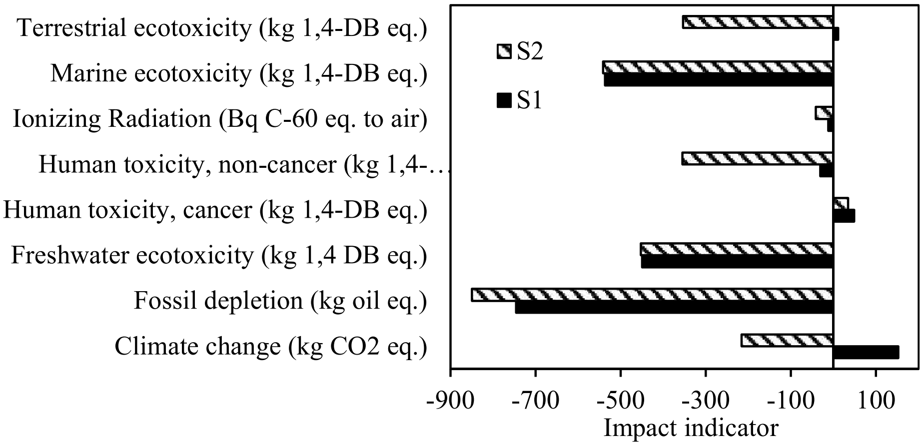


Figure 6.3.2. *The environmental impacts of pyrolysis of PET-12 including WCNTs synthesis (S2) and excluding WCNTs synthesis (S1)*

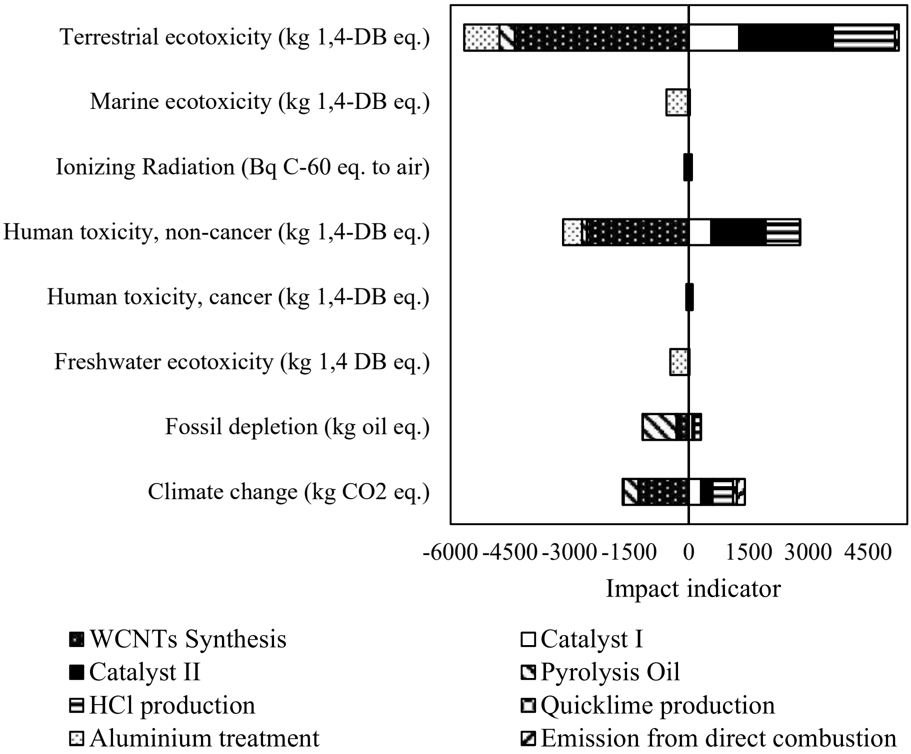


Figure 6.3.3. *The environmental impacts of integrated pyrolysis process (S2) illustrating the individual contributions of the major products and processes*

The advancement of human toxicity (cancer) and ionizing radiation potentials for S2 were 30 and 248%, respectively, when compared to S1. The extraction and synthesis of zeolite and other chemicals in the catalyst I preparation footprint were one of the major contributors to the environmental impacts in both the scenarios. The synthesis of WCNTs accrued additional benefits to the S2 apart from the pyrolysis oil produced in both scenarios. The marine and freshwater ecotoxicity potentials exhibited insignificant differences between S1 and S2. The prevention of wastewater discharge from the aluminium recovery process was the predominant contributor for the benefits associated with the marine and freshwater ecotoxicity potentials. Apart from the climate change potential, the terrestrial ecotoxicity and human toxicity (non-cancer) generated the greatest benefits for S2 when compared to S1. The extraction and production of chemicals used in the preparation of catalyst and HCl applied in washing the CNTs were the major contributors for the impacts. Nickel sulphate amounted to 99% of the environmental impacts associated with the preparation process of catalyst II in both the impact categories. Urea (18 and 8%), iron chloride (29 and 31%), and zeolite (52 and 60%) were the significant contributors to the terrestrial ecotoxicity and human toxicity (non-cancer) potentials, respectively, associated with the preparation process of catalyst I. The synthesis of WCNTs in S2, and pyrolysis oil production and treatment process of aluminium in S1 and S2 were the predominant contributors to the benefits.

Terrestrial acidification as well as freshwater and marine eutrophication potentials were insignificant for both the scenarios due to the trace phosphorous, sulphur and nitrogen discharge from the system. The usage of metal-based catalysts contributed to the metal depletion potential (2.91 Kg Cu-equivalents). The remaining impact categories, including land use, freshwater consumption, stratospheric ozone depletion, fine particulate matter formation, and photochemical ozone formation were determined to be insignificant.

Three different WCNTs yields, including 1, 2.4 (obtained yield) and 4%, were applied to evaluate the sensitivity of the product yield on the integrated pyrolysis process (Figure 6.3.4). The benefits accrued improved proportionately with increases in the WCNTs yield. A critical yield of >2% WCNTs is essential to obtain positive impacts on human toxicity (non-cancer), climate change, terrestrial ecotoxicity, and ionizing radiation potentials. However, over 4% yield of WCNTs is required to entirely offset the human toxicity (cancer) potential. The most sensitive impact categories were terrestrial ecotoxicity and human toxicity (non-cancer). Fossil depletion potential progressively reported enhancement in environmental benefits of −675, −850 and −1062 Kg oil eq. for 1, 2.4, and 4% yield of WCNTs, respectively. The influence of different WCNTs yield on marine and freshwater ecotoxicities were minimal. In conclusion, the importance of WCNTs yield to the integrated pyrolysis process was accentuated by the sensitivity analysis.

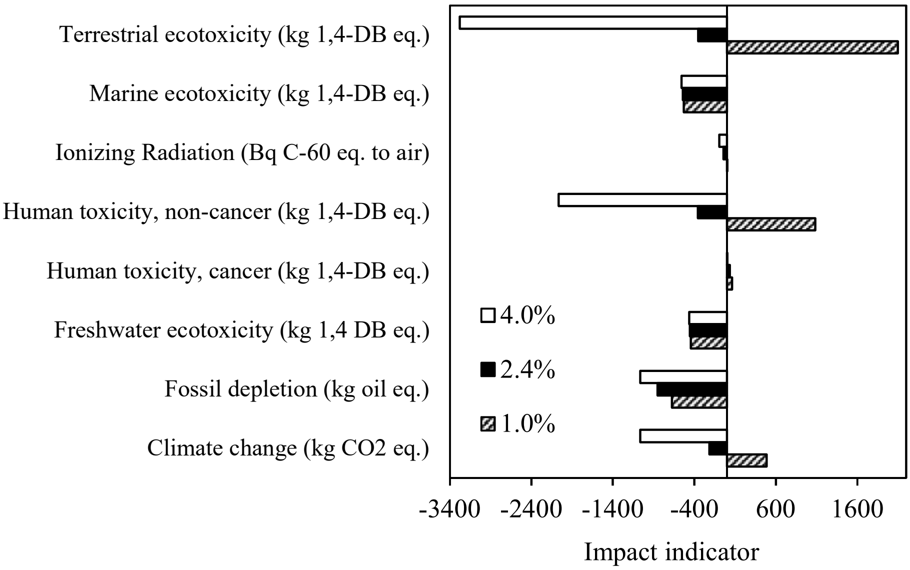


Figure 6.3.4. *The influence of different yields of WCNTs from the integrated pyrolysis process as determined by the sensitivity analysis*

One of the superior contributors in offsetting the environmental burdens incurred was the pyrolysis oil with 68.3% yield from the integrated pyrolysis process. Although deficient for some impact categories, including human toxicity (non-cancer) and climate change potentials, the pyrolysis oil product negated a considerable burden associated with the system. Further addition of the synthesis of WCNTs from non-condensable gas augmented significant benefits. The effective benefit of WCNTs synthesis from pyrolysis of plastics is the displacement of the virgin hydrocarbon (i.e., acetylene) consumed during the conventional synthesis of CNTs. The benefits can be further amplified with improvements in the WCNTs yield, as demonstrated by the sensitivity analysis. The development of superior conversion mechanisms, including improved WCNTs/catalyst II and WCNTs/feedstock yields, and recirculating the effluent non-condensable gas, could assist in achieving enhanced environmental benefit along with reduced flue gas emissions and increased carbon capture for the system. Furthermore, an increase of 9-times higher magnitude of H_2 was obtained from the fuel gas discharged after WCNTs synthesis when compared to the non-condensable pyrolysis gas. Therefore, an additional extraction step could be included for H_2 as a by-product and accrue additional environmental benefits to the integrated pyrolysis process in future studies.

Notably, the human toxicity (cancer) potential demonstrated environmental burden despite the synthesis of WCNTs and therefore, further enhancement of the process is essential to offset the associated burden. The application of zeolite-based catalyst I contributes considerably to the human toxicity potential. Therefore, effective reuse or regeneration of the catalyst I could alleviate this burden. Although multiple regenerations were reported [144], the efficacy depreciated subsequently [150, 151]. Hence, further advancement and testing of the catalyst I, including its regeneration potential, would add significant value. Conversely, the associated environmental footprint of the catalyst I in the integrated pyrolysis processes could be alleviated by successfully substituting the use of metal-zeolite catalyst with incineration ash residue. Although the environmental footprint could be reduced by synthesizing catalyst from waste resources, the catalytic activity still requires enhancement to be equivalent with metal-zeolite catalysts.

In conclusion, the environmental benefits affiliated with the synthesis of WCNTs from non-condensable pyrolysis gas that was derived from FPPW feedstock was paramount. One of the important advantages of the synthesis of WCNTs from FPPW is the displacement of fossil feedstock used for conventional CNTs synthesis. Moreover, the integration of synthesis of WCNTs with the existing pyrolysis system could facilitate additional economic revenue stream and contribute significantly towards the treatment of plastic waste over alternate recycling methods.

6.3.2.2. Effect of plastic feedstock

The environmental implications of utilizing the following feedstocks for the WCNTs synthesis were compared (Figure 6.3.5):
Scenario A (S-A): conversion of PET-12 to WCNTs and pyrolysis oil
Scenario B (S-B): conversion of PET-28 to WCNTs and pyrolysis oil
Scenario C (S-C): conversion of MVP to WCNTs and pyrolysis oil
The by-products, including coke, char and fuel gas, were combusted under all three scenarios. The correlation was conducted for the material flows in the system in order to delineate the leverage exerted by the differences in the material composition. The energy flow was disregarded for all the scenarios as it was identical. Except the ecotoxicity potentials, the environmental burden quantified by all the impact categories was greater for S-B when equated with S-A. The primary reasons for the inferior environmental benefit were due to the reduced yields of WCNTs and pyrolysis oil (Table 6.3.1), and the reduced plastic fraction in the PET-28 feedstock due to the presence of

10.7% aluminium, when analysed with respect to S-A. Moreover, the presence of greater PET content in PET-28 further contributed to the climate change potential via direct CO_2 emission. Contrarily, the recovery of 10.7% aluminium in S-B enhanced the environmental benefits of aquatic (marine and freshwater) and terrestrial ecotoxicity potentials by 190 and 9%, respectively. The avoidance of the wastewater discharge in conventional treatment process of aluminium is accredited for the accrued benefits.

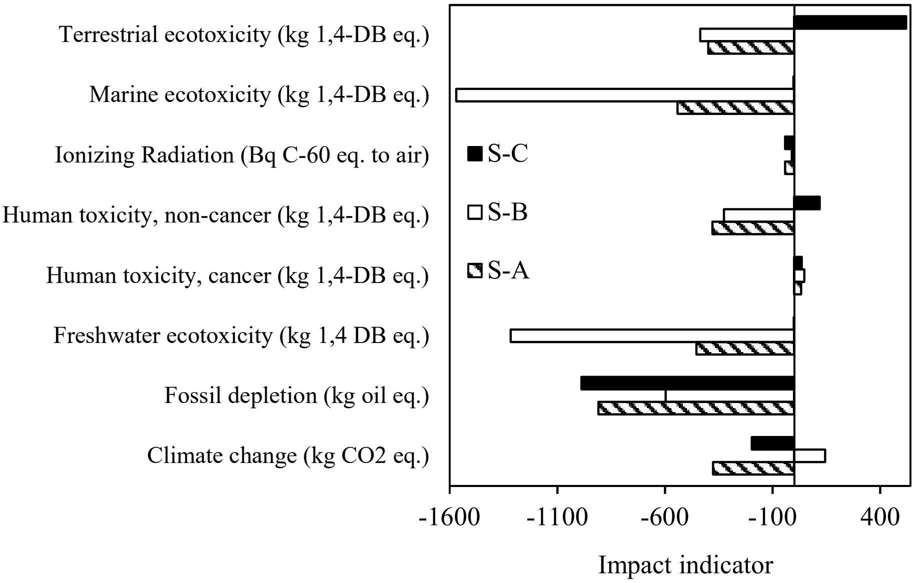


Figure 6.3.5. *The results obtained on the environmental impacts of different plastic feedstock, including PET-12 (S-A), PET-28 (S-B) and MVP (S-C), for the integrated pyrolysis process*

The S-A demonstrated commensurate benefits for all the impact categories when compared to S-C, except the human toxicity (non-cancer) and the ecotoxicity potentials. The outcome suggested the insignificant influence of contaminations, including ink, adhesive and food residues that existed in the FPPW during pyrolysis process. Nevertheless, the catalytic activity could be affected by the impurities, necessitating further research. Although the WCNTs yield were comparable for both the scenarios, the yield of pyrolysis oil was minimized in the S-A feedstock by the presence of 3.6% aluminium, which lowered the carbon content available for conversion. Contrarily, the climate change, human toxicity (non-cancer), and ecotoxicity potentials were reduced by the aluminium recovery. Moreover, the municipal plastic waste could be a potential feedstock for the integrated pyrolysis process supported by the analogous experimental and environmental efficiency of the MVP feedstock when compared to PET-12.

The pyrolysis treatment process was unaffected by the difference in the feedstock composition and type. For example, PET-28 feedstock with significantly high PET content was examined as a worst-case scenario of FPPW. Although the yield of the products varied depending on the original content of plastics in the feedstock, the properties of the derived products was consistent. It highlights the versatility of the pyrolysis process in treating various types of municipal plastic waste. The advancement and complexity of the synthesis of pyrolysis oil from plastic waste are discussed in detail elsewhere [34, 47, 145, 152, 153]. In conclusion, the application of low PET feedstock was less detrimental to the environment and accrued greater benefits than the high PET FPPW. The outcome of MVP and FPPW was analogous in most impact categories. Furthermore, the potential in the treatment of a disparate mixture of plastic waste through the integrated pyrolysis process has been demonstrated.

6.3.2.3. Limitations and recommendations

The data for synthesis of CNTs that is extrapolated from lab-scale experimental results is one of the central limitations of the LCA. Therefore, the incorporation of data from the commercial synthesis process of CNTs would furnish a more precise result on the environmental impacts. The other limitation is the 60% loss of heat energy input for the pyrolysis process as waste heat in the adopted literature data [143]. It could be rectified by improving the efficiency of design and infrastructure to minimize the heat loss of the system. Furthermore, the application of process data from industrial-scale mass production system could reduce the overall energy consumption of the integrated pyrolysis system [154].

One of the considerable contributors to the negative impacts was the utilization of catalysts. Therefore, the environmental burdens could be minimized with the development of catalysts from waste resources as explored in the previous chapter (Chapter 6.2) with MSW incineration ashes. Furthermore, the development of suitable catalysts to facilitate the conversion of all the primary pyrolysis vapor, including condensable and non-condensable, to WCNTs could significantly improve the environmental and economic benefits. Additionally, the integrated process prevents the depletion of natural and fossil resources by averting the use of virgin feedstock in the synthesis of high-value product.

In conclusion, the upcycling of FPPW to WCNTs and pyrolysis oil was demonstrated as beneficial from the environmental perspective and improves the circularity of the material flow. The outcome of the LCA aided in recognizing definite targets for further advancements from the environmental perspective. Furthermore, the application of the integrated pyrolysis process would aid in the development of circular economy and diminish the reliance on fossil resources. The next chapter demonstrates the application of the synthesized WCNTs in electrochemical sensing.

6.4. LCA of the material choices in electrochemical sensor application – a comparison with waste-derived carbon nanotubes

In this chapter, the LCA of the application of the WCNTs is compared against various other material selection in voltammetric sensing using screen-printed electrodes (SPEs). A comparison with real commercial product such as SPEs provides a comprehensive insight into the avoided materials and the extended benefits of synthesizing the CNTs from waste. The portable, user-friendly and field-deployable electrochemical instrumentation in on-site detection of target analytes have expedited the development of voltammetric sensors [155-157]. The superior sensitivity of voltammetric sensors are useful in food safety, biomedical analysis, and environmental monitoring applications for the trace level determination of analytes, including drugs, toxins, pesticides and heavy metals [158-160]. A three-electrode system, including a reference electrode (RE), counter electrode (CtE) and working electrode (WE), is the predominant measurement setup of voltammetric sensors [161, 162]. The principle of voltammetric sensing involves the measurement of the current between CtE and WE as a result of oxidation/reduction of the analyte at the WE when changing (sweeping) the potential between RE and WE [158-163].

The quality and type of electrode materials applied for the WE significantly influence the electrochemical performance of voltammetric sensors. Initially, the highly reproducible, renewable and smooth surface of the liquid drop mercury electrode was a favoured electrode material (EM) [164]. However, the environmental and health hazard of mercury electrodes were immense. Numerous non-mercury EMs, including noble metals (such as gold and platinum) and carbon materials (such as glassy carbon and carbon nanomaterials) were applied with the progressive advancements in electroanalytical field [155, 165, 166].

One promising approach for the voltammetric sensor production is screen-printing methodology [167-169]. The electrodes are fabricated by the application of EM paste through a stencil design of patterned metal mesh. The mass production of single-use, low cost, and disposable voltammetric sensors with superior reproducibility could be achieved by the automation of the screen-printing methodology [168, 170]. Figure 6.4.1 depicts a typical design of an SPE with three-electrode system, including RE, CtE and WE, printed on a single substrate surface. A considerable reduction of the required sample amount, superior flexibility with a wide range of EM configurations, and elimination of pre-treatment steps (including polishing and cleaning) are the predominant advantages of disposable SPEs over conventional electrode systems [169, 171, 172].

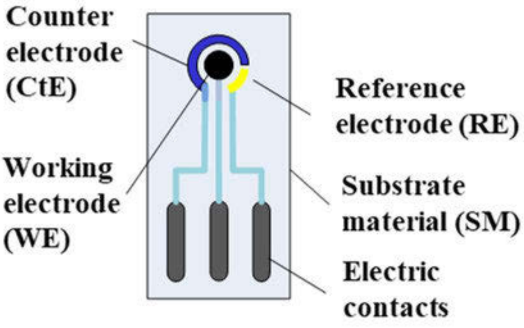


Figure 6.4.1. *A typical design of the screen-printed electrode (SPE) based voltammetric sensor*

Substrate materials (SMs) and EMs are the two main components in SPEs (Figure 6.4.1). In most cases, SMs account for the greatest weight fraction in SPEs as it serves as the platform for the electrode components. Ceramic, glass, plastic, textile and paper are the most common SMs applied in SPEs [173], due to their suitable physical and chemical properties, including inertness, temperature stability, and insulating characteristic [159, 174, 175].

Stable REs are chiefly fabricated with Ag/AgCl, while WE and CtE are frequently made from carbon pastes in SPE based voltammetric sensors due to minimal background currents, wide potential windows, and low cost [170, 176]. Furthermore, the electric contacts in SPEs are commonly made of Ag, due to its superior conductivity. Additionally, modification to the WE surface is applied by depositing electrocatalytic materials on it in order to considerably enhance the sensor signal. The prominent electrocatalytic materials are metal nanoparticles (such as platinum, gold, silver and copper) and carbon materials (such as carbon black, carbon nanotubes and graphene), which benefits by improving the surface to volume ratio, conductivity, adsorption property, and signal intensity and minimizing the background current in voltammetric sensors [177-180]. Notably, the CNTs have gained significant acceptance among the scientific research community due to its superior electrochemical detection of different analytes [180-182]. Further enhancement to their physicochemical characteristics can be attained by introducing functional groups (including hydroxyl, carboxylic and carbonyl) [183, 184].

The environmental impacts of SPEs needs evaluation due to the predominantly single-use characteristic and the scope of the quantum of measurements recorded using SPEs. The environmental footprint and sustainability of the application of SPEs relies upon the selection of appropriate component materials, including SMs and EMs. Importantly, scarce natural resources are often commonly used in burgeoning applications such as SPEs. In the context of finite natural resources and its assimilation potential, the prevailing environmental footprint of humankind is unsustainable [185]. Therefore, the objective of this LCA is to determine the environmental footprints of the production and end-of-life of different material selection in SPE application, including EMs (platinum, gold, silver, copper, carbon black, CCNTs and WCNTs) and SMs (cotton textile, HDPE plastic, kraft paper, glass and ceramic). The most eco-friendly combinations of SMs and EMs are identified. Furthermore, the functionality of WCNTs in SPEs is validated by comparing it with CCNTs.

6.4.1. Life cycle modelling

The goal of LCA is to compare the environmental footprint of the different material selection of SPE components. The scope of LCA incorporates all the unit operations involved in the production of materials, including extraction of resources, primary production, energy consumption, and emissions associated with the sub-processes. The FU of LCA was defined as the production of 1 kg of the material. The system boundary covered the production processes of every material alternative.

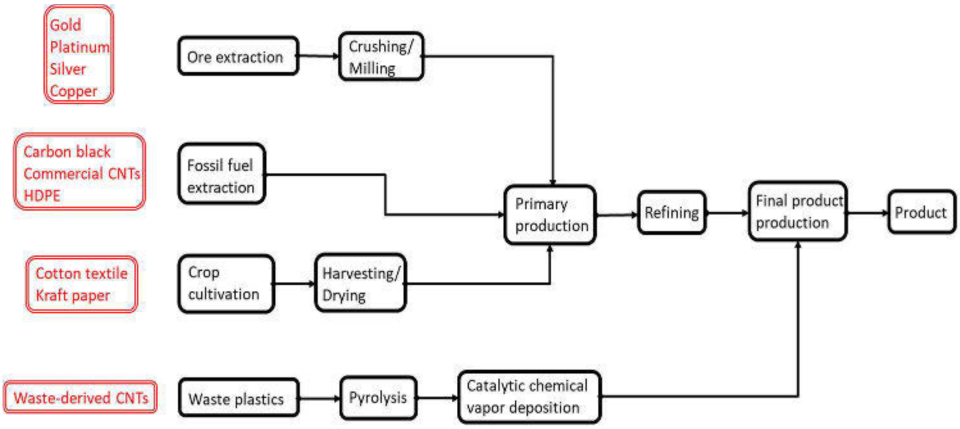


Figure 6.4.2. *The production process flow chart of the studied selection of electrode and substrate materials in SPEs*

The assumption of hypothetical scenario was discounted in this LCA to prevent the associated uncertainties, as the SPEs are still a novel technology with immature industrial-scale manufacturing processes and supply chains, and undetermined constitutional applications, unlike the grocery bags in Chapter 6.1. Therefore, this LCA is focussed on the comparison of the production processes, which has been highlighted as the significant contributor in similar LCAs and represents the paramount concern [**Paper I,** 186-188]. The production of nanoforms was excluded from the LCA due to (i) the divergent manufacturing methods involved for distinct materials, (ii) the private licenses protecting the respective manufacturing process and associated data, (iii) the difficulties in substantiating the lengthened lifespan of materials/products, (iv) the challenges associated with measuring the actual functional advantages, (iv) the complications in estimating the averted burdens, anticipated benefits, and allocating the displaced products, and (v) the difficulties in considering the uncertain environmental and toxicological consequences.

6.4.2. Life cycle impact assessment results and discussion

Seven EMs, including platinum, gold, silver, copper, carbon black, CCNTs, and WCNTs and five SMs, including cotton textile, HDPE plastic, kraft paper, glass and ceramic, were assessed as the components of SPEs. The production processes of various materials differ from mining and extraction to farming, despite the application in SPEs were synonymous. The end-of-life fate under various waste treatment methods are presented for all the EMs and SMs. Furthermore, in order to ensure compatibility, a comparison of voltammetric detection of different heavy metals between CCNTs and WCNTs is provided.

6.4.2.1. Environmental impacts of the production of various electrode materials

The environmental impacts, including the 19 impact categories, of EMs are presented in Figure 6.4.3. Gold yielded the greatest environmental impacts in marine (18079 kg 1,4-DB eq.), freshwater (13521 kg 1,4-DB eq.) and terrestrial ecotoxicities (132101 kg 1,4-DB eq.), human toxicity (cancer) (21328 kg 1,4-DB eq.), human toxicity (non-cancer) (4167907 kg 1,4-DB eq.), land use (2254 annual crop eq.·y), freshwater (505 kg P eq.) and marine eutrophication (8 kg N eq.) potentials. Long term inorganic emission to freshwater and heavy metal emissions to freshwater and air are attributed to the environmental effects. Moreover, the gold fraction in ore is frequently low. Therefore, immense amount of ore is enforced to be extracted and processed to produce one unit of gold that amplifies the resource and energy consumption when compared to other ordinary metals [189]. The disposal of sulfidic tailings from extraction and refining processes during bulk processing contribute significantly to the ecotoxicity potentials [186]. Similarly, platinum demonstrated the greatest environmental impacts in climate change (including (26839 kg CO_2 eq.) and excluding (27017 kg CO_2 eq.) biogenic carbon), fossil (8408 kg oil eq.) and metal depletion (9072 kg Cu eq.), fine particulate matter formation (625 kg $PM_{2.5}$ eq.), and terrestrial acidification (2113 kg SO_2 eq.) potentials eclipsing gold. The application of fossil energy resources and elements and the associated inorganic emissions to air were the contributors for environmental impacts. Furthermore, platinum and gold yielded analogous environmental impacts in freshwater consumption, stratospheric ozone depletion, ionizing radiation, and photochemical ozone formation (ecosystem and human health). The superior ore quality and greater reserve of silver precipitated diminished effects on the environment. The impacts on marine eutrophication and stratospheric ozone depletion were insignificant for all the EMs. The least environmental effects among metals was generated for copper due to the relative affluence of copper. The effects were negligible in all the impact categories except terrestrial ecotoxicity (1645 kg 1,4-DB eq.) and human toxicity (non-cancer) (747 kg 1,4-DB eq.). However, the scope of application of copper is restricted due to its oxidative nature and sensitivity to chemicals when compared to other EMs.

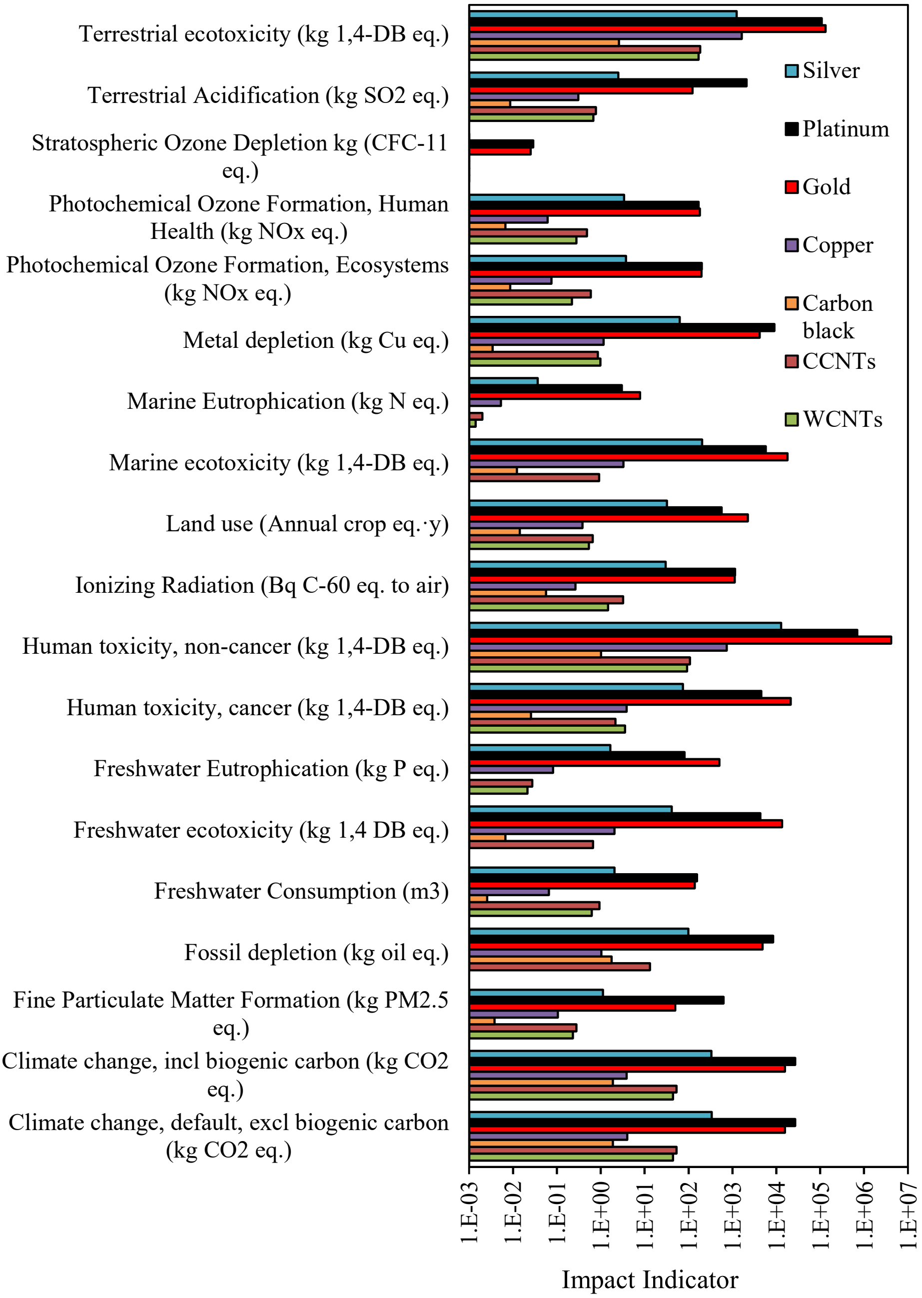


Figure 6.4.3. *The impact assessment results comparing the production footprint of WCNTs with the other predominant EMs*

Among all the EMs, the lowest impact was observed for carbon black in all the impact categories except fossil depletion potential (1.8 kg oil eq.).

Importantly, positive effect was generated for WCNTs in the impact categories, including marine (−21.64 kg 1,4-DB eq.) and freshwater (−18.21 kg 1,4-DB eq.) ecotoxicities and fossil depletion (−22.13 kg oil eq.) potentials (not shown in Figure 6.4.3). The positive effect was attributable to the by-product (pyrolysis oil), which yielded superior benefits than the associated fossil resource consumption during the integrated pyrolysis process (Chapter 6.3 and **Paper III**). Moreover, WCNTs demonstrated smaller environmental impacts in all the impact categories except metal depletion and human toxicity (cancer) potentials when compared to CCNTs. Therefore, carbon black and WCNTs are prescribed as the suitable EM selection for SPE application. Specifically, RE and CtE could adopt carbon-based EMs to avert the use of metals, while Ag is an essential EM for REs except where pseudo-RE is applicable.

Importantly, it is necessary to shift towards carbon-based materials as the noble metals, including gold, platinum and silver, are finite resources and eventually deplete over long term utilization. Fourteen metals were listed as scarce, comprising the metals extracted from high-grade ores, the United States' list of conflict materials, and the European Union's list of critical metals, by Arvidsson and Sanden [190] upon examining sixty elements from the periodic table. Platinum, gold and silver that were included in the list are commonly applied in SPEs. Excessive usage of scarce metals would lead to permanent resource depletion-driven scarcity, which present a possible insecurity to the modern development [191]. Hence, in order to advance towards the sustainable development goals, exclusion of the usage of scarce resources at the preliminary phase of a product evolution is imperative. Conversely, carbon-based materials, including the WCNTs, can be classified as a boundless reserve, comparatively, provided sustainable measures are practiced.

6.4.2.2. Environmental impacts of the production of various substrate materials

The environmental footprint of SMs are assessed to compare different materials and recommend a suitable combination of EM and SM from an environmental perspective, as it constitutes a significant portion of the SPEs. The impact assessment results for the production of cotton textile, HDPE plastic, kraft paper, glass and ceramic are presented in Figure 6.4.4. Cotton textile exhibited the greatest environmental impacts in all the impact categories when compared with the other SMs. The elaborate production process, comprising intensive farming and manufacturing activities, and the application of fertilizers and pesticides as highlighted in Chapter 6.1 (and **Paper I**) are the reasons for the greater environmental footprint of cotton textile. The fossil depletion potential was predominantly influenced by the utilization of non-renewable energy resources for all the SMs. Adopting renewable energy resources in the entire value chain would surmount the associated impacts. Human toxicity (cancer (94%) and non-cancer (86%)) and terrestrial ecotoxicity (90%) potentials were contributed by the emissions to freshwater and heavy metal emission to air during the cotton textile production, respectively. The second greatest impact in fossil depletion and climate change potentials was exhibited by HDPE plastic due to the utilization of fossil fuels in material extraction and production processes. The climate change potential (excluding and including biogenic carbon) for kraft paper was 1.5 and −0.52 kg CO_2 eq., respectively. Nevertheless, in order to allocate the benefits of biogenic carbon, sustainable production practices are essential. Kraft paper and ceramic exhibited second greatest impacts in the case of both human toxicity potentials and similar effects in terrestrial ecotoxicity potentials.

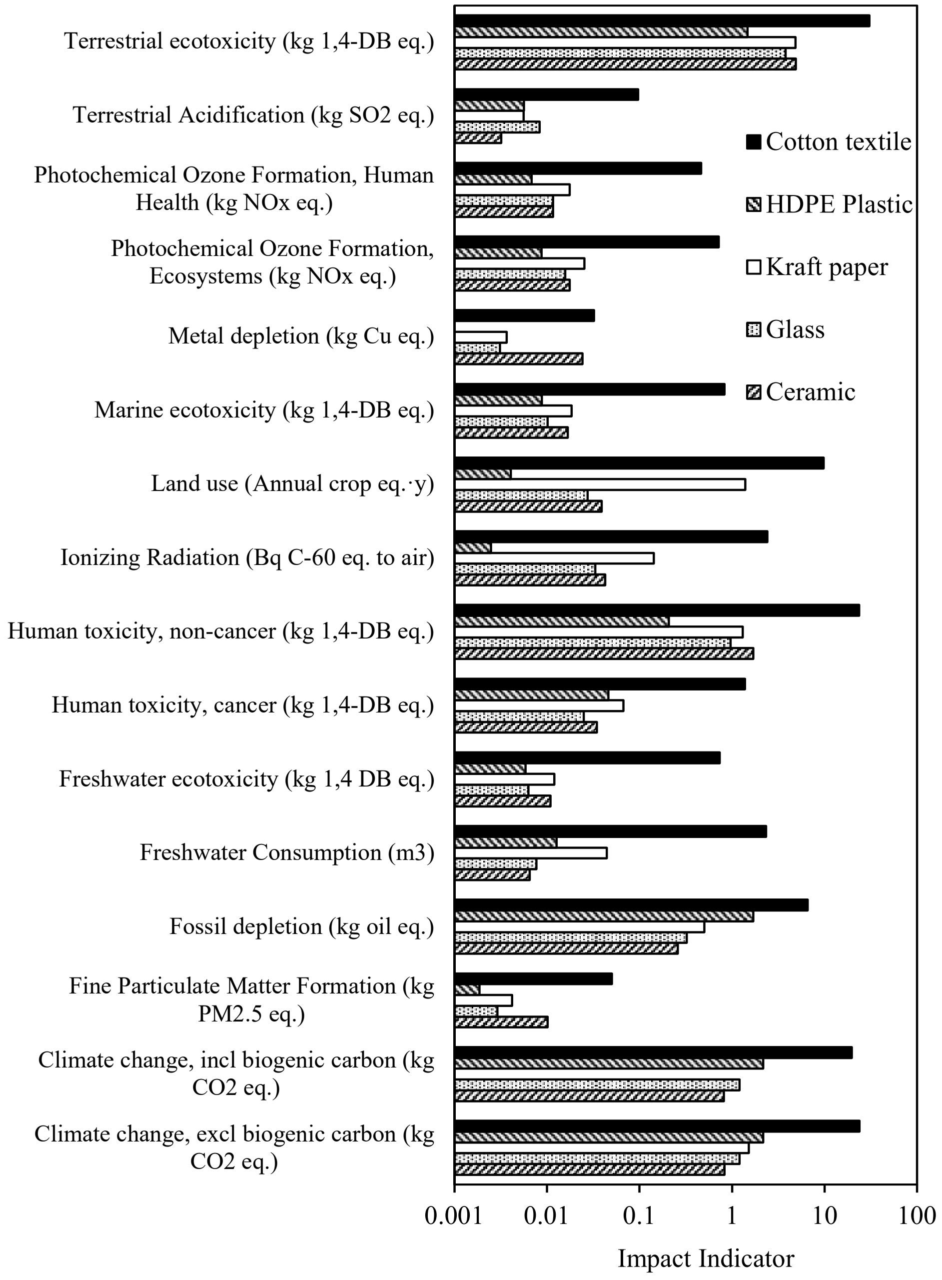


Figure 6.4.4. *The impact assessment results of the production of various SMs used in SPEs. Marine and freshwater eutrophication and stratospheric ozone depletion potentials were below 0.001 for all the SMs.*

Cotton textile exhibited the greatest impact in ionizing radiation, freshwater consumption, and land use change potentials, due to the consumption of voluminous quantities of water and use of extensive area of farm lands.

Fertilizers for crop cultivation and consumption of fossil fuel for material processing are the predominant contributors for ionizing radiation. Kraft paper yielded the second greatest effects in land use, freshwater consumption, and ionizing radiation potentials. The significant land usage in kraft paper and cotton indicates the relatively greater demand of land area for timber production and crop cultivation, respectively, when compared to the remaining alternatives. The impacts of ceramic, glass and plastic were minimal in these impact categories when compared to paper.

The environmental impacts of the remaining impact categories demonstrated a similar trend with the greatest impacts generated from cotton textile in all the categories. A notable fine particulate matter formation (0.0102 Kg $PM_{2.5}$ eq.) and metal depletion (0.0242 Kg Cu eq.) potentials were ascertained to ceramic. In conclusion, the least impact in 13 out of 19 impact categories was yielded by HDPE plastic. All the remaining alternative materials exhibited a lower impact of few orders of magnitude when compared to cotton textile. The observed results were analogous to the case of grocery bags (Chapter 6.1), which concluded the HDPE plastic bags to be the recommended option. Therefore, the order of preference for the selection of SM is plastic, ceramic, glass, paper and cotton, based on the upstream production processes. Furthermore, the specific application requirement would further determine the utilization of materials. For example, in application requiring flexible materials, plastic or paper SMs can be utilized rather than ceramic or glass and vice versa.

6.4.2.3. End-of-life assessment

In order to trace the fate of WCNTs after SPE application, subsequent end-of-life assessment was conducted and suitable options are discussed in comparison with the alternative materials. Especially in the case of single-use materials or products like SPEs, the evaluation of end-of-life release is appropriate as it corroborates the disposal practices [186]. The prevailing international solid waste management practices, including incineration, open burning, and landfilling, or leakage into the natural environment are the potential end-of-life fate of SPEs. Table 6.4.2 presents the comprehensive assessment of the physical fate of the EMs and SMs in the environmental sinks. The atmospheric emissions were disregarded due to the short-lived nature of the air-borne particles of SPEs.

Landfilling and incineration are appropriately deliberated in determining the fate of the EMs and SMs when compared with other environmental sinks.

Incineration provides near complete decomposition of the carbon-based materials. For example, incineration presumably eliminates carbon black under optimal stoichiometric condition via complete combustion to form CO_2 [192, 193]. Analogously, carbon-based nanomaterials decompose completely at 740°C under oxidative conditions [194, 195]. The CO_2 discharge of carbon black, CNTs, cotton textile, HDPE plastic, and kraft paper are 3.67, 3.67, 1.62, 2.24 and 1.51 kg CO_2 eq./kg of the material, respectively upon complete combustion (Chapter 6.1). The remaining materials refrain to contribute to direct CO_2 release from incineration due to their non-carbon origin. The metal particles accumulated in the slag, bottom ash, and separated fraction from the exhaust gases, while about 1% is discharged into the environment as particulate emission [192, 196]. Ceramic and glass are retained chiefly in the bottom ash or slag as they are inert and non-flammable. Conversely, the SMs and EMs are retained indefinitely in the landfill, except cotton and paper that decompose overtime and fragmentation and redistribution of plastic due to the weathering effects. The redistribution of weathered fragments might percolate the soil and surface waters via groundwater and leachate runoff potentially leading to toxic effects on organisms. Open burning inflicts analogous transition of EMs and SMs as in incineration. However, the deficiency of exhaust treatment in open burning amplifies the atmospheric emissions resulting in possible terrestrial acidification, climate change, photochemical ozone formation, and fine particulate matter formation effects. Moreover, the assessment of the environmental impacts of open burning is complicated due to the formation of incomplete combustion products.

Table 6.4.2. *The fate of various EMs and SMs of SPEs in different environmental sinks*

EM/SM	Incinera-tion	Landfill	Open burning	Surface water	Soil
Platinum	Inert	Inert	Inert	Inert	Inert
Gold	Inert	Inert	Inert	Inert	Inert
Silver	Inert	Inert	Inert	Inert	Inert
Copper	Inert	Inert	Inert	Inert	Inert
Carbon black	Combust	Inert	Combust	Inert	Inert
Carbon nanotubes	Combust	Inert	Combust	Inert	Inert
Cotton textile	Combust	Biodegrade	Combust	Biodegrade	Biodegrade
HDPE plastic	Combust	Inert*	Combust	Inert*	Inert*

Kraft paper	Combust	Biodegrade	Combust	Biodegrade	Biodegrade
Glass	Inert	Inert	Inert	Inert	Inert
Ceramic	Inert	Inert	Inert	Inert	Inert

†Inert: remain physically inert for >100 years; Biodegrade: can decompose in <1 year.

*Due to the weathering effect there is a possibility of plastic fragmentation and micro-plastic formation.

Depending on the ash content of the respective materials, ash residue will be present in most of the combustible materials.

As highlighted in the introduction, **Reviews I** and **II**, the plastics and nanomaterials in the environment could pose undetermined consequences in the environment, particularly the ecotoxic effects. The impacts are presently being studied and there has been enormous focus on this research area. For example, the acute toxicity (24-72 h) of five types of plastic leachates from 26 commercial products was tested on *Daphnia magna* [197]. HDPE products instilled toxic effect from 1 among the 5 tested samples, while plasticized polyvinyl chloride (PVC) and epoxy demonstrated acute toxicities from all the samples. Conversely, acrylonitrile butadiene styrene, rigid PVC, and PP caused minimal leachate toxicity. The reasons for toxic effect was attributed to the cationic metals and hydrophobic organics. Similarly, the acute toxicity of different types of leachates from ground plastics of commercial products was tested in *Nitocra spinipes*, in comparison with leachate from tire as positive control [198]. At high concentration (liquid/solid ratio: 10), 38% of the plastic leachates induced toxic effects. The influence of water hardness and plastic nanoparticle functionality was examined for the cellular adsorption by algal cell walls [199]. The toxicity of plastic nanoparticles was influenced by the application of suitable dosimetry that factors agglomeration, specific materials properties, adsorption behaviour, and cellular attachment potential. Therefore, diverse toxic effects were observed in different types of plastics.

Conversely, administration of high dosage of CaO-SiO$_2$-P$_2$O$_5$-B$_2$O$_3$ glass ceramics to female and male Sprague-Dawley rats exhibited no observed systemic toxic effect from a 90-day intravenous toxicity study [200]. However, different concentration of silica infused calcium phosphate glass injected intraperitoneally into C57BL/6 mice for 30-days reported higher mortality rates with increasing silica concentration in glass [201]. The dissolution of Si^{4+} was attributed to the toxic effects of glass and ceramic. Nevertheless, cotton and paper are considered biocompatible materials that undergo biodegradation in the environment.

The EMs are predominantly utilized in micro- or nano-forms, which reported greater toxic effects towards organisms [202, 203]. The toxicity of the nanomaterials, including carbon nanomaterials [204-206], gold [207, 208] and silver [209-212], have been extensively researched and reviewed. CNTs incorporated electronic memory devices exhibited negligible environmental effects when compared with metals and production footprint of CNTs, and indicated minimal impacts of carbon nanomaterials in nano-enabled devices. The non-nano emissions from CNT synthesis, including upstream production of energy and materials, exhibited several orders of magnitude greater aquatic ecotoxicity than the effects of direct CNT discharge into the environment [213]. The toxicity of nanomaterials on human health and organisms are challenging to assess, complicated to examine, and inconclusive to forecast [211, **Review II**], which are significantly influenced by environmental factors including the effects of weathering. Moreover, the toxicity potential research on copper [214-217] and platinum nanomaterials [218-220] requires further investigation. The apprehensions related to the environmental impacts are aggravating as growing number of nano-enabled products penetrate the commercial applications. Appropriate waste treatment for nanomaterials are essential to control the environmental effects and address the imminent problem [221]. An exhaustive review of the fate, exposure, physico-chemical transformations, and toxicities of various engineered nanomaterials and future directions are presented in **Review II** to address the existing research gaps.

Therefore, carbon black and WCNTs are endorsed as the appropriate EMs for SPE utilization, due to the greater environmental footprint of metals, end-of-life impacts, and diminished scope of metal recovery. Among all the SMs, plastics reported minimal impacts overall, which is recommended when the end-of-life treatment option is incineration or other thermochemical methods (including pyrolysis). For example, the application of pyrolysis would perpetually recirculate a portion of the carbon back into the material flow. However, the experimental validation is essential to verify the circularity of the carbon flow. There could be possible interferences with the presence of impurities, including other electrode components and sample residues (for example, heavy metals in case of environmental monitoring application), which justifies the need for further investigations. However, the application of SPEs might not be as confined or controlled as in the case of plastic bags in metropolitan areas (Chapter 6.1 and **Paper I**). Therefore, ceramic, glass or paper substrates are alternately prescribed as a low risk environmental friendly SM option. The recommendation is mainly attributed to the associated end-of-life waste management practices. In conclusion, a combination of any of the prescribed EM and SM would signify an environmentally friendly selection in voltammetric application of SPEs. The material options are accessible depending on the specific requirements of SPEs. For example, flexible SMs, including plastic or paper, are applicable in wearable sweat analysis, while rigid SMs are sufficient in environmental monitoring. However, carbon-based electrodes, including carbon black or WCNTs, can be adopted for WE and CtE in most cases in order to minimize the environmental footprint, while RE predominantly require Ag. Therefore, an environmentally sensitive design and material selection is essential in the development of SPEs and application of WCNTs in order to mitigate the associated environmental impacts.

6.4.2.4. Comparison of electrochemical performance of CCNTs and WCNTs

Despite the WCNTs were determined as superior in terms of environmental benefits compared to CCNTs, their voltammetric performance with SPEs requires validation. Hence, the voltammetric sensing potential was evaluated for various heavy metals, including Ag^{+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}, in order to substantiate the application of WCNTs as a replacement for CCNTs in SPEs. The toxic and persistent nature of the heavy metals establishes them as crucial elements in environmental monitoring [222].

The WE was modified with CNTs for the voltammetric measurement using expendable SPEs made of ceramic SM (DRP-C110, Metrohm). Silver paste was used to imprint RE and electric contacts, while carbon paste was applied for inscribing CtE and WE. The modification to WE was conducted by adding WCNTs or CCNTs (5 mg) into a 10 mL mixture solution comprising 2 mL isopropanol and 8 mL DMF (Merck Pte. Ltd., Singapore) and sonicated for 10 min. Subsequently, 10 µL of sonicated suspension was deposited on the WE and dried at 60 °C for 7 min in a hot air oven. The CCNTs and WCNTs incorporated SPEs were labelled as CCNTs-SPCE and WCNTs-SPCE, respectively. Differential pulse anodic stripping voltammetry (DPASV) was applied to evaluate the electrochemical detection behaviour of heavy metals on the modified voltammetric sensors using a handheld potentiostat (µStat 300 Bipotentiostat, Metrohm). A detailed protocol of the DPASV measurement is provided in **Paper IV**. The detection of heavy metals on the SPE chip involved depositing 100 µL of sample solution.

WCNTs-SPCE obtained greater signal strength and reduced background current for all the heavy metals when compared to CCNTs-SPCE (Figure 6.4.5). The potential reasons include formation of a smooth WE surface with greater surface-to-volume ratio for the modification with WCNTs, thereby promoting the kinetics of electron transfer, signal strength, and adsorption properties of the voltammetric sensors. Conversely, the CCNTs aggregated and formed heterogenous deposition on the WE surface when compared to WCNTs, resulting in unstable response signals and greater background current. Therefore, the WCNTs indicated potential to substitute CCNTs, due to its superior voltammetric sensing performance. Further applications of WCNTs in electrocatalytic oxygen reduction and modified-WCNTs in near real-time analysis of para-cresol in wastewater were reported in Veksha et al. [79] and Zhao et al. [184].

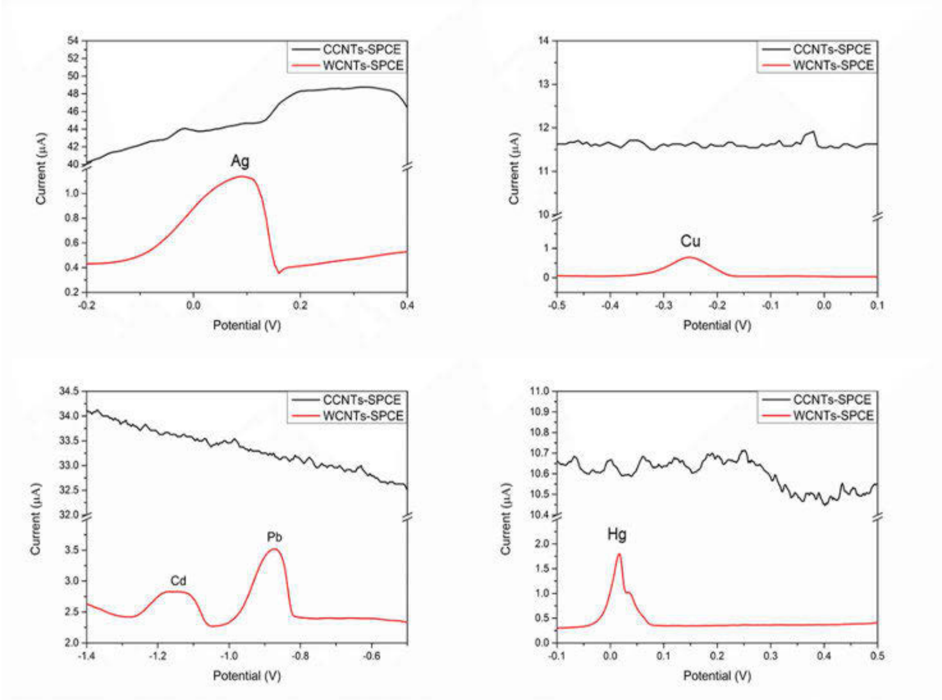


Figure 6.4.5. *Determination of various heavy metal ions with voltammetric sensors using SPEs: Typical DPASVs of heavy metal ions (50 ppb, in 0.1 M acetate buffer, pH=4.5) with WCNTs and CCNTs modified SPE chips. Acetate buffer solution (prepared by adjusting the different ratio of 0.1 M acetic acid and 0.1 M sodium acetate) was used to dilute 1000 ppm standard solutions of Ag, Cu, Cd, Pb, and Hg from PerkinElmer Inc. (Waltham, MA, USA) to the concentration of 50 ppb.*

6.4.2.5. Limitations and recommendations

The LCA is limited to the primary production of materials, due to (i) the early stages of development of commercial SPEs, (ii) unavailability of data or privately restricted/licensed/protected production methods, and (iii) variations in methods involved in sub-processes by the specific manufacturers and applications. Conducting full LCA is challenging for novel products due to the data gaps and limited industrial-scale manufacturing. Furthermore, the interaction of nanoparticles with molecules in the environment is excluded. For example, the toxicity potential could be influenced by the interactions of metal nanoparticles with different flue gases from end-of-life incineration treatment [223]. Nevertheless, the LCA specifically highlights the imminent adverse impacts of the various materials selection for SPEs.

Noble metal EMs demonstrated significantly greater environmental impacts among all the EMs. A shift towards carbon-based EMs is necessary to reduce the environmental footprint. Furthermore, the application of metals in single-use miniature sized product would designate the recycling of it challenging, despite the metals being absolutely recyclable natural resources. The prevailing mechanical and electromagnetic separation and extractive metallurgy techniques would require further development for the case of SPEs. Importantly, the failure to facilitate numerous reuses of metals would signify underutilization of the resource intensive production processes of metals. Moreover, the complex composition of SPEs, scattered distribution of the product, impurities from the sample residues, and inadequate concentration of the recoverable materials, designates SPEs challenging to recycle. Conversely, the affluence of carbon reserves determines the transfer from scarce resources advantageous [190]. The materials with equivalent functional properties and inferior embodied energy of refining and extraction when compared to noble metals would be the suitable alternative to minimize the environmental impacts [186, 224]. Additionally, metal extraction relies on the availability of ores, which are confined to specific geographical locations and their geopolitical influences, while carbon-based materials are devoid of such externalities. Therefore, the carbon-based SPEs are prescribed with reverence to their abundance and favourable end-of-life management options.

The market projections for SPEs remain positive and complacent with growing number of applications. The electrochemical sensor market was valued at US$ 6.19 billion in 2019, with a predicted compound annual growth rate of 11.4% and market valuation reaching US$ 11.83 billion by 2025 [225]. The likelihood of commercial application is indicated by the market projections and thereby, provide a preview of the possible environmental releases. For example, millions of units of blood glucose monitors are utilized everyday across the world [226]. Analogously, daily sweat analysis monitors are expected to enter commercial application in professional sporting and recreational activities and point-of-care healthcare services [227-230]. These examples strongly indicate the possibility of immense amount of resource utilization and waste generation, which can be contoured at the early stages of development through LCA. Therefore, the exceptional potential applications of SPEs were the reason for conducting LCA of SPEs by incorporating the WCNTs from integrated pyrolysis process (Chapter 6.3 and **Paper III**). The utilization of fossil-based resources can be avoided by adopting to the WCNTs or other waste-derived carbon nanomaterials. Furthermore, the application of waste-derived materials would encourage further maturation of the integrated pyrolysis technology and adoption of industrial-scale waste treatment facilities, which would further depreciate the life cycle footprint of WCNTs production. Thereby, the ultimate benefits would include, the advancement of productive waste treatment technologies, averting the utilization of fossil resources, and achieve greater recycling rates.

7. Conclusion and closing remarks

This research work assessed the life cycle of the plastic waste, its treatment in the form of upcycling to a novel product (CNTs), and subsequent application of the waste-derived CNTs (WCNTs). Herein, the presented works cover a comprehensive life cycle of virgin plastics to combustion and energy recovery at the end of its second life cycle (i.e., WCNTs). Initially, the life cycle implications of a widely consumed plastic packaging product i.e., plastic grocery bags were presented. In comparison with other alternatives in the case of Singapore, plastics fared better in terms of environmental footprint. The study underscored the indispensability of case specific evaluation of the environmental implications for managing plastic waste. In a well-designed confined metropolitan waste management system, where end-of-life thermal treatment is practised and the leakage of waste into the natural environment is negligible, using plastics would be the environmentally friendly option. Shifting to cotton or paper grocery bags would aggravate the negative environmental effects, including eco-toxicity and global warming potentials. The concluded results may be appropriate for cities such as Singapore, Amsterdam, Hong Kong, Frankfurt, Tokyo and Dubai, where the waste management practice can theoretically be tightly controlled and leakage of waste into the natural environment can be restricted. Minimizing the overall consumption is the best option, followed by opting for reusable plastic bags. The results implied that plastics could continue to be employed in urban centres, due to its inherent advantages and extensive availability.

As a plastic waste treatment method, the thermochemical upcycling of plastic waste via pyrolysis is a technologically innovative and simultaneously economical option. The experimental results and LCA of the pyrolysis of plastics and upcycling to CNTs were reported. The incineration ashes from MSW treatment demonstrated potential to be employed as a low-cost environmentally friendly catalyst for upgrading of volatile products during plastic pyrolysis. A selective production of BTEX oil compounds were achieved by the incineration ashes when equated with the control experiments. In comparison to the benchmark metal-zeolite catalyst, the Ni-loaded ash catalysts contributed to the improvement of the overall oil fraction while reducing the gas fraction. However, the oil product yielded lower BTEX compounds and gasoline-like fraction for Ni-loaded ash catalyst than the metal-zeolite catalyst's yield. In the case of gas products, the Ni-enriched catalysts favored the formation of hydrogen and short-chain hydrocarbons, while simultaneously reducing the C3- and C4-alkenes. This study demonstrated the catalytic potential and reported an exploratory investigation of the utilization of ash in catalytic reforming. Therefore, further pre-treatments, including size fractionation, refining, chemical treatment, and modifications, are necessary for the full development of the ash catalysts. The study opens an avenue for testing and development of MSW incineration ashes in pyrolytic applications. Successful replacement of the reliance on synthetic or natural catalysts, including zeolites, with catalyst developed from incineration ash could accrue considerable environmental and economic advantages. However, for the LCA study, a metal-zeolite catalyst with commensurately greater environmental footprint was selected in order to substitute the oil product with commercial quality fuel.

An extensive LCA was conducted to environmentally validate the synthesis of CNTs and oil from pyrolysis of plastic. The environmental benefits of adding a CNT synthesis process to the conventional pyrolysis were highlighted. Additionally, various FPPW feedstocks were studied for comparison. The LCA study demonstrated that the plastic pyrolysis process integrated with WCNTs synthesis provides considerable environmental advantages in terms of climate change, human toxicity (non-cancer and cancer), fossil depletion, ionizing radiation, and terrestrial eco-toxicity potentials. A sensitivity analysis of various WCNTs yields emphasized the range of effects that a waste treatment facility synthesizing a high value product could impart to the environment. The environmental benefits proportionately increased with higher yields. Furthermore, feedstock with low PET content was less impactful on the environment and accumulated greater benefits out of the waste management system when matched against high PET and displayed equivalent performance to the feedstock with MVP in most impact categories. Moreover, divergent fractions of plastic waste can be treated with the integrated pyrolysis process (including WCNTs synthesis) demonstrating its versatility. In conclusion, the integrated pyrolysis process enhances the environmental sustainability and revenue stream of the conventional pyrolysis process, substitutes the alternative requirement for plastic waste disposal including landfilling and incineration, and abnegates the consumption of fossil fuel resource in conventional CNTs production. Importantly, the integrated pyrolysis process provides circularity to the material flow by recapturing the otherwise wasted carbon back into the product system as WCNTs and pyrolysis oil. The subsequent application of the WCNTs in voltammetric determination of heavy metals was reported. WCNTs achieved lower background current and superior signal intensity for the heavy metal ions when compared to CCNTs, making it a viable alternative for CCNTs in commercial application.

Finally, an LCA of the material selection of the SPEs revealed the extended benefits of WCNTs application beyond the commonly perceived scope of waste-derived materials. The electrode materials exhibited environmental impacts that were several orders of magnitude greater than the substrate materials when assessed per unit of the material. Among all the materials studied, platinum and gold reported the highest environmental implications, owing to the intensive mining and processing activities. The environmentally friendly option would be averting the usage of metals as highlighted in this study. Specifically, the carbon-based electrode, including carbon black and WCNTs, is recommended over the metal electrodes wherein the efficiency would not be compromised. The order of preference is carbon black, WCNTS, CCNTs, silver and gold/platinum. The most environmentally friendly option for SPEs in voltammetric sensing applications would be a combination of carbon-based EM and either plastic, ceramic, glass or paper SM. Although Ag is required in most REs, carbon black or WCNTs could be used in CtE and WE in order to curtail the use of metals and thereby, the environmental footprint. Notably, the existing options of incineration or other thermal treatment are greatly applicable for the end-of-life waste management of carbon-based electrodes. Importantly, WCNTs were produced from waste resources that are abundant, economical, carry low or negative environmental footprint, and demonstrated comparable voltammetric performance to the commercial CNTs. Advancement to the industrial scale production of WCNTs could further lower their environmental footprint. Hence, in order to alleviate the associated environmental impacts and achieve the sustainable development goals, an environmentally sensitive design and material selection in SPEs are crucial.

Overall, the research thesis reported an integrated life cycle assessment of the plastic material from production to end-of-life, upcycling treatment of the plastic waste to CNT and oil synthesis, and the application of the upcycled WCNTs product. It provides a context for the extended benefits of the plastic waste derived high value materials like CNTs. A clear technological and economical value of the circular economy concept can be realised from the environmental perspective by moving towards an integrated approach. We ascertain that similar studies are rare and are indispensable in future research works to advance towards a truly circular economy.

The results reported herein are governed by the LCA models, data quality, and assumptions. The computed results may vary depending on the deviation of the input data. Nevertheless, the obtained results provide a valid perspective of the environmental implications of the plastic bags and their alternatives, plastic waste treatment to high value WCNTs, and application of WCNTs in electrochemical sensing.

The focus areas for advancement in sustainable product manufacturing can be delineated by LCA [187]. The application of LCA at the early research stage would facilitate greater influence on the product and process design with the necessary flexibility to enforce considerable changes [71]. It also prevents enormous economic expenditures incurred when the switch to alternate materials occur at the later stages due to sustainability concerns. Minimizing the environmental footprint of every product is of paramount importance to address the growing environmental concerns from a global perspective. The global risk report 2020 [231] predicted that the environmental risks are the greatest in terms of impact and likelihood when compared to the geopolitical, societal, economic and technological risks.

Moreover, the proposed integrated pyrolysis technology in this research is scalable in the context of the metropolitan cities, where the waste management system is well controlled and require local treatment. It also ensures the soil and marine littering are minimized. The United Nations projected that approximately 60% of the global population will reside in urban settlements [89]. The intensifying efforts towards improving global sustainability demands documenting environmental impacts at different scale of effects and embracing sustainable practices. Furthermore, an exponential increase of the cost of the materials ensue as the finite resources depletes gradually. Therefore, the economic deprivation of the material emanates ahead of the substantial physical depletion [191, 232]. Hence, the transformation towards sustainable and renewable material and energy resources and supply chain is crucial to ensure the unhindered long-term utilization of any material. Therefore, the benefits of the conclusions drawn in this thesis would be realized when the wider movement towards sustainability by various stakeholders across the world intensifies. The LCA based decisive evaluation would assist in focused initiatives for waste prevention, reduction of environmental footprint, effective resource management and recovery, and informed policy decisions.

The global plastic waste generation has grown dramatically. The mismanagement of plastic waste has raised numerous environmental concerns. Therefore, this serves as a critical juncture to address the concerns of plastic waste disposal. Hence, the development of new upcycling technologies that are environmentally, industrially and economically feasible is paramount. Based on the series of LCA studies, this integrated pyrolysis process with WCNTs synthesis demonstrated potential as one such novel upcycling technology. The research and full-scale development of such technologies should be supported by the governments considering the enormous prospects of the successful and scalable solutions. Thus, the novel integrated pyrolysis process may find application in large-scale plastic waste management.

8. References

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ISBN 978-952-12-4080-5