On the Synthesis of Carbon Nanotubes from Waste Solid Hydrocarbons

A Dissertation Presented

by

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Abstract

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. They consist of coaxial tubular graphene sheets, with diameters in the order of nanometers ($1 \times 10^{-9}$ m) and lengths in the order of micrometers ($1 \times 10^{-6}$ m). The latter can now be extended into the order of meters. Carbon nanotubes (CNTs) have been studied for more than 20 years. CNTs possess superior electrical, mechanical, thermal, chemical, and structural properties, which make their potential applications nowadays overwhelmingly widespread. Now entering into the growth phase of product life cycle, increasing usage of CNTs in commercial products is part of the beginning of the nano-technological revolution. Expanding markets for CNTs' large volume applications place ever-increasing demands on lowering their production costs to the level acceptable by the end-user applications. It is estimated that the mass application of CNTs will be facilitated only when the price of CNTs approaches that of conductive carbon black.

The synthesis of CNTs involves three elements: the carbonaceous feedstocks (raw materials), the catalysts, and the necessary process power consumption. Therefore, they jointly contribute to the major operation expenditures in CNT synthesis/production. Current technologies for large-scale production of CNTs (either chemical vapor
deposition, CVD, or combustion synthesis) require intensive consumption of premium feedstocks and catalysts, and the CVD process requires high energy consumption. Therefore, there is a pressing need for resource-benign and energy-benign, cost-effective nano-manufacturing processes. In the search for sustainable alternatives, it would be prudent to explore renewable and/or replenishable low-cost feedstocks, such as those found in municipal, industrial, and agricultural recycling streams. In the search for low cost catalysts, stainless steels have been proposed as cost-effective dual purpose substrates and catalysts, as they contain transition metals (iron, nickel, etc.) which are well-documented to be effective catalysts for CNT growth.

In this doctoral dissertation, the feasibility of utilizing municipal / industrial / agriculture wastes as carbon sources for CNTs has been examined and proven. It was also found that the effluents of the CNT synthesis process can also serve as gaseous fuels for “clean” power production, which can then be used for energy self-sustaining CNT synthesis. Besides, a facile catalyst pre-treatment has been developed to activate stainless steel based substrate/catalyst for efficient CNT growth. Finally, the efforts of CO$_2$ on the pyrolyzate gases and on the CNT co-generation were also investigated.
Dedication

To my wife: Jing Wang
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Introduction

The goal of this study is to investigate and document a potentially sustainable waste up-cycling pathway, which provides both fuel and value-added CNTs, with the lowest possible costs in terms of energy and resources. CNTs consist of coaxial tubular graphene sheets, with lengths in the order of micrometers ($1 \times 10^{-6}$m) and diameters in the order of nanometers ($1 \times 10^{-9}$m). [1-3] Carbon nanotubes (CNTs) have been studied for more than 20 years since being reported by Ijima.[4-6] The appealing electrical[7-9], mechanical[10-15], thermal[7, 16-18], chemical[19-21], and structure [22-24] properties of CNTs lead to numerous applications, such as supercapacitor electrodes[25-60], transparent conducting films[61-67], field emission displays[68-80], LCDs and OLED-based displays[57, 81-96], fuel cell electrodes[97-145], structural composites[146-154], photovoltaic devices[155-193], aerospace and automobile applications[194-210], etc.. These value-added CNT materials are currently produced at a global annual rate of 3,500 tons, with a projected annual production growth rate of 30.6%[211]. Expanding markets place ever-increasing demands on lowering their production costs.

This doctoral dissertation was inspired from past work elsewhere and in this laboratory on the synthesis of CNTs, and on the treatments of solid plastic wastes, which are seemingly unrelated. It had been reported that the synthesis of CNTs consumes hydrocarbons in gas phase, and effective process temperatures were in the broad neighborhood of 800 °C[212-214]; it had also
been reported that solid plastics could be converted into gaseous hydrocarbons through pyrolytic gasification (pyrolysis), and the maximum gas yield (around 95%) could be obtained again in the neighborhood of 800 °C[215, 216].

Therefore the following scientific hypotheses were used to guide this thesis:

(i) since pyrolytic gasification of solid waste plastics at around 800°C generates hydrogen and light hydrocarbons, the latter can then be used as carbon donor gases for CNT synthesis, and

(ii) if pyrolytic gasification is followed by mixing of the gaseous pyrolyzates with oxygen to generate, upon ignition, a fuel-rich premixed flame, then the effluents of that flame can also be used as carbon donor gases and the flame can generate heat to sustain the CNT synthesis process.

There are three elements involved in CNT formation: carbon donor gases, energy supply, and catalysts. Current technologies for CNT generation require intensive consumption of premium feedstocks and, often, of costly catalysts; they also require input of external energy [217]. Industrial-scale production of CNTs is typically achieved through chemical vapor deposition (CVD) methods [218, 219], which consume a variety of expensive premium chemical feedstocks, such as methane[220, 221], ethylene [222, 223], carbon monoxide (CO) [224-226] and hydrogen (H₂) [225]; or by flame synthesis techniques[227], which also consume premium feedstock fuels. Additionally, CVD methods are energy-intensive[228-230]. Thus, this work addressed the
pressing need for developing resource-benign and energy-benign, cost-effective nano-
manufacturing processes.

Given that fossil fuel resources are finite and are widely projected to dwindle in the not too
distant future, it is imperative not only to increase the efficiency of fossil fuel use but, also, to
identify alternative energy sources and to develop technologies for their effective use. Searching
for sustainable alternatives to fossil fuels, it is prudent to also explore readily-available low-cost
fuels found in municipal / industrial / agricultural waste streams. For instance, 5% of the current
US petroleum consumption is used to generate plastics (30 million tons per year!), most of which
are discarded and, unfortunately, are non-biodegradable. Since only a small fraction (7%) of
plastics are recycled, due to limited markets and limited consumer compliance, most end up in
landfills or generate ubiquitous litter (consider for instance the Great Pacific Garbage
Patch[231] and the plastics accumulation in the North Atlantic Subtropical Gyre [232]).

Besides the ever-increasing amounts of waste polymers, there are also ever-increasing amounts
of process waste biomass. Such biomass is a by-product of production of alternative fuels, such
as bio-alcohols and bio-diesels, which have been recently in high demand since they are viewed
as renewable clean-burning and carbon-neutral energy resources, with the potential of replacing
large amounts of petroleum-derived transportation fuels [233, 234]. Nowadays the demand for
bio-fuels production is rapidly increasing, and this also increases the volume of the associated
waste process residues that need disposal. As an example, Brazil that produces bio-ethanol and
sugar from sugarcane, consumed more than 630 million tons of this crop in 2009 and generated
approximately 142 million tons of waste bagasse as a solid process residue[235]. Other countries,
like US, produce bioethanol mainly from corn, resulting in a process residue termed dried distillers grains with solubles (DDGS), after the starch fraction of corn is fermented with selected yeasts and enzymes to produce bio-ethanol and carbon dioxide [236-238]. The amount of DDGS produced in the US was about 32 million tons in 2009 [239].

![Diagram of waste-to-energy and CNT up-cycling process.](image)

**Figure 1: Targeted waste-to-energy+CNT up-cycling process.**

These solid hydrocarbon wastes can serve not only as sources for alternative fuels because of their high heating values, but also as carbon donors for CNTs because of their carbon-rich content. Generating value-added products, such as CNTs, from recycled plastic wastes (together
with other feedstocks) is thought to enhance the motivation for recycling, lower the cost of the CNT products and, in turn, help overcome the hurdles of their large-scale use in consumer and industrial applications.

Aside of the aforementioned carbon feedstock and energy requirement, catalyst is the third element involved in CNT formation, and also a key determining factor of the production cost of CNTs. Efforts have been made to explore low cost catalyst options, and stainless steels (SS) have been proposed as good candidates. SS contains transition metals (iron, nickel, etc.) which are well-documented to be effective catalysts for CNT growth [240-242]. For instance, type 304 SS is readily-available and reasonably-priced, its application as catalyst is of technological interest to CNT manufacturing.[243, 244] Besides, SS can be used in templates of various geometries (porous block,[245] wire cloth (mesh),[246] tubing,[247] plate,[248, 249] etc.). This facilitates applications where direct interaction between CNTs and conducting substrates are desirable,[243, 248, 250] as well as the applications where the architectures of templates can serve as the structures.[251, 252] However, having a passive film of chromium oxide on its surface, SS does not readily react with gaseous hydrocarbons, which are common carbon growth agents for CNTs. This is why pre-treatment of SS is usually necessary to breach its outer protection layer.

This doctoral dissertation investigated a) the feasibility of utilizing municipal / industrial / agriculture wastes as carbonaceous feedstocks for carbon nanomaterials (CNTs), as well as sources for generating alternative fuels, b) the factors affecting this waste up-cycling pathway with emphasis placed on the CNT formation, and c) facile catalyst preparation/pre-treatment methods. This process pyrolyzed solid wastes (post-consumer plastics, tires, and biomass
residues, such as those from the bio-ethanol industry) into a multi-component fuel stream and high-value CNTs. Waste plastics and tires are non-biodegradable and are in need of reuse markets; process biomass is renewable and may be considered “carbon-neutral”. Feedstocks examined were waste plastics (polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyethylene terephthalate (PET)), as well as agriculture residuals (sugarcane bagasse and distiller’s dried grains with solubles (DDGS)) and unserviceable tires. Fundamental investigations were conducted to understand the aforementioned up-cycling process, the reaction chemistry therein, the roles of carbon donors, as well as the effects of CO₂ addition on the pyrolysis and the CNT synthesis processes.

The dissertation has been organized in eight chapters:

**Chapter 1** reviews prior work on converting polymers into carbon-based nanomaterials.

**Chapter 2** describes the synthesis of CNTs from polyethylene using a pyrolysis–combustion technique. Pre- or post-consumer polyethylene (in strips, pellets or ground particles) was pyrolyzed to gaseous products, which were then combined with an oxygen-containing gas and auto-ignited to create a fuel-rich flame. The combustion effluent was used to synthesize multi-wall CNTs using stainless-steel wire mesh as both catalyst and substrate.

**Chapter 3** addresses the production of CNTs by catalytic conversion of wastes from the bioethanol industry, in the form of either sugarcane bagasse or corn-derived distillers dried grains with solubles (DDGS). Both bagasse and DDGS were pyrolysed at temperatures in the
range of 600-1000 °C. The pyrolyzate gases were then used as CNT growth agents by chemical vapor deposition on stainless steel meshes, serving as both catalysts and substrates.

**Chapter 4** demonstrates the synthesis of CNTs by up-cycling common solid wastes. These feedstocks could supersede the use of costly and often toxic or highly flammable chemicals, such as hydrocarbon gases, carbon monoxide, and hydrogen, which are commonly used as feedstocks in current nanomanufacturing processes for CNTs. Agricultural sugar cane bagasse and corn residues, scrap tire chips, and postconsumer polyethylene (PE) and polyethylene terephthalate (PET) bottle shreddings were either thermally treated by sole pyrolysis or by sequential pyrolysis and partial oxidation.

**Chapter 5** focusses on the pretreatment of the catalytic substrate, in the form of 316L SS wire mesh, needed for effective CNT formation from pyrolyzate gases of polyethylene and polystyrene, i.e., a mixture of hydrocarbons and hydrogen.

**Chapter 6** studies the effect of adding CO₂ on the thermal decomposition of the major polyethylene pyrolyzate (ethylene) and on the subsequent catalytic formation of CNTs. The results were interpreted with the assistance of reaction kinetics.

**Chapter 7** summarizes the work conducted in this dissertation, and

**Chapter 8** lists suggestions for future work.
References:


[125] Fujigaya, T., M. Okamoto, and N. Nakashima, *Design of an assembly of pyridine-containing polybenzimidazole, carbon nanotubes and Pt nanoparticles for a fuel cell*


CHAPTER ONE

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1. Up-cycling Waste Plastics into Carbon Nanomaterials: A Review

Abstract

Polymer production and utilization are currently widespread and have greatly improved people's standards of living. However, due to their stable and nonbiodegradable nature, postconsumer polymers pose challenging issues to the environment and ecosystems. Efforts are being made not only to contain the generation of polymer wastes and associated littering but, also, to find ways of utilizing them sustainably. Aside from mechanical recycling, which turns postconsumer polymers into new polymer products, and thermal recycling, which releases the thermal energy contained within waste plastics through combustion, chemical recycling converts waste polymers into feedstock for chemicals/materials/fuels production. This manuscript reviews prior work on a special application of the particular chemical recycling route that converts polymers into carbon-based nanomaterials. These materials feature extraordinary physical and chemical properties with tremendous applications potential. However, their production processes are both resource- and energy-intensive. Yet, by taking advantage of the high carbon content of waste polymers, as well as of their high energy content, a cost-effective, environmentally-friendly, and self-sustaining production of carbon nanomaterials can be achieved.
1.1 Introduction

1.1.1 Plastic Wastes Overview

Figure 2: World production of plastics in 2012, with their typical applications in E.U. and the U.S.A. Data cited from Refs. 1 and 2.

Over the past 50 years the proliferation of nonbiodegradable man-made materials, such as plastics, has increased dramatically. Major applications of plastics include but are not limited to packaging, building and construction, transportation/automotive, and electrical and electronic components. As illustrated in Figure 2, the world production of plastics in 2012 reached a record high, 280 million tons, roughly two-thirds of which were contributed jointly by China (~23%), European Union (EU-27, 21%), USA (16%), and Japan (5%).[1] Correspondingly, more than 25, 31, 28, and 9 million tons of plastic wastes were generated in Europe,[1] USA,[2] China,[3] and Japan,[4] respectively.
1.1.2 Plastic Waste Management – Conventional Recycling Solutions

As most polymers are mass-produced and low-priced, they are readily discarded after use. Waste management is needed to minimize the plastic wastes and to reduce their environmental impacts, and typically, waste reduction, recycling (mechanical, chemical, and thermal) as well as landfilling are considered as common solutions.[5, 6] There are issues related with landfilling, however, such as those of (a) continuously decreasing available landfill space and (b) ubiquitous littering causing land and water pollution. Consider for instance the accumulation of plastics refuse in the North Atlantic Subtropical Gyre,[7] as well as the Great Pacific Garbage Patch,[8] where the amount of nonbiodegradable wastes (such as plastics and rubber) has increased for more than 100 times in the past 40 years.[9] Further increases in recycling and reuse are therefore not only desirable but rather essential in addressing the aforementioned issues.

Recycling is to collect waste materials, process or re-manufacture them (either biologically, mechanically, chemically, or thermally) into new products, and to market those products (making the wastes recycled).[10] Biological recycling takes place at the presence of microorganisms, such as bacteria, fungi, and enzymes, to degrade the plastics,[11-13] whereas mechanical-, chemical-and thermal-recycling are human activity based. Table 1 summarizes the related terms and definitions used by different countries/regions on these human-activity-involved recycling. Mechanical recycling processes plastic wastes (mainly thermoplastics, e.g. PE, PP, PET) into secondary raw material (termed recyclate) for common plastics.[14] No significant changes in the chemical structures occur during
mechanical recycling. It starts with materials collection, followed by identification, sorting, grinding, washing, drying, separating, agglomerating, extruding/compounding, and eventually pelletizing. Chemical (or feedstock) recycling partially converts some plastics into their monomers, or into hydrocarbon fractions, which can then be used either as feedstock for polymerization, or in other chemical processes. Thermal recycling takes advantage of the high energy content of the plastic wastes (as they are hydrocarbons in nature, which will be discussed latter), and recovers the energy through thermal processes (sometimes also called incineration, or waste-to-energy conversion).

Recycling enables substitution of raw materials with postconsumer materials, which would otherwise be obtained from increasingly scarce natural resources, such as metals or petroleum, in cases of both feedstock materials and input fuels. Therefore, recycling is one of the favorite methods in the waste management hierarchy. However, the rate of global recycling is still not as high as it would be economically and environmentally desirable, and it varies in different geographical areas. Japan has the highest recycling rate (78%, 2011),[4] followed by EU,[1] (59%, 2011) and China (48%, 2011),[3] while U.S. has the lowest recycling rate (EPA 8%, 2011, does not include the parts being recycled through combustion).[2] Thermal recycling (energy recovery) and mechanical recycling are the predominant methods nowadays,[15] while chemical (feedstock) recycling is significantly utilized only in limited countries (areas), such as in Japan. There are many factors that jointly lead to such low recycling rates, including: (1) the lack of access to recycling facilities,[16] (2) the complexity of waste identification, separation and
cleaning,[17, 18] and (3) the limited municipality and consumer compliance and the limited markets for the recycled plastics.[19]

### Table 1: Summary of Plastics Recycling Methods.

<table>
<thead>
<tr>
<th>International Standard Organization (ISO) 15270</th>
<th><strong>Japan</strong></th>
<th><strong>EU</strong></th>
<th>American Society for Testing and Materials (ASTM) International D7209 – 06</th>
<th>Methods, Cited from Reference¹⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical recycling</td>
<td>Material recycling</td>
<td>Mechanical recycling</td>
<td>Primary recycling</td>
<td>Recycling isolated/segregated plastics to make (primary) plastic raw materials / products</td>
</tr>
<tr>
<td><strong>Chemical recycling</strong></td>
<td>Chemical recycling</td>
<td>Monomerization / Feedstock recycling</td>
<td>Tertiary recycling</td>
<td>Monomerization</td>
</tr>
<tr>
<td><strong>Energy recovery</strong></td>
<td>Thermal recycling</td>
<td>Thermal recycling</td>
<td>Quaternary recycling</td>
<td>Blast furnace reducing agent</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Coke oven chemical feedstock recycling</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Gasification / Liquefaction</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Chemical Feedstock</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fuel</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cement kiln</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Waste power generation / incineration / Refuse Derived Fuel / Refuse Paper &amp; Plastic Fuel</td>
</tr>
</tbody>
</table>
Public awareness, government legislation, and technology improvements in the recent past have partly addressed this problem.[19] However, as recycled plastics often have compromised properties, they cannot be used in their original applications.[20] Recycling therefore may not be treated as a sustainable solution by itself, especially taking into account that such efforts are affected largely by the overall economics: the recycling market is cyclic and depends on the strength (and viability) of the economy.[20] Identifying high-capacity markets for recycled products is problematic, thus creation of a new market for recycled plastics, particularly leading to high-value products, would be desired to spur interest in recycling and reuse of such polymers. It will also then be beneficial for the recycling markets, the associated infrastructure and, eventually, the public's mindset for recycling.

1.1.3 Plastic Waste Management—Advanced Upcycling Solutions

It is well known that the products of chemical recycling are majorly hydrocarbons, which can be used either as fuels for power generation, or as feedstocks (such as monomers) to produce new materials. It has been suggested that, in the traditional chemical industry process, raw materials account for 60% to 90% of production costs,[21] thus inexpensive feedstocks yielded from chemical recycling enable a new pathway to lower the cost of manufacturing value-added products. The processes involved herein will then be termed "upcycling" process, as the quality/value of the final products is upgraded, and there are studies and reviews on related topics, such as upcycling plastics into chemicals for monomer feedstock,[22-27] fuels,[22, 28-33] etc. Due to the fact that carbon is the major constituent of plastics (see Table 2), the waste plastics can therefore provide a carbon source for carbon-based value-added products.
Table 2: Carbon Contents in Major Commercial Polymers (Plastics)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular formula</th>
<th>Carbon Content (in wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (PE)</td>
<td>(C₂H₄)ₙ</td>
<td>85.6</td>
</tr>
<tr>
<td>Polypropylene (PP)</td>
<td>(C₃H₆)ₙ</td>
<td>85.6</td>
</tr>
<tr>
<td>Polystyrene (PS)</td>
<td>(C₈H₈)ₙ</td>
<td>92.2</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>(C₁₀H₈O₄)ₙ</td>
<td>62.6</td>
</tr>
<tr>
<td>(PET/PETE)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacrylonitrile (PAN)</td>
<td>(C₃H₃N)ₙ</td>
<td>67.9</td>
</tr>
</tbody>
</table>

Such products include but are not limited to light hydrocarbons,[34-37] carbon black/activated carbon,[38] carbon fibers,[39, 40] fullerenes,[41-43] carbon nanotubes,[44-48] and graphene.[49] Nowadays, there are various applications of graphite and carbon black at annual production rate exceeding 1 million tons. Meanwhile, there are certain carbon allotropes being considered as advanced materials, as they possess unique properties, in nanoscale, leading to unprecedented functions with numerous applications. Examples of these carbon allotropes include, but are not limited to: nanodiamond, fullerene, carbon onion, carbon nanotubes, and graphene, see Figure 2. Therefore converting waste plastics into such value-added products is an excellent example of upcycling.
This study will focus on the efforts, made in recent years, to explore ways of upcycling plastic wastes into carbon nanotubes (CNTs), a category of fullerenic materials. The background of CNTs will be introduced first, including their types, properties and applications. Typical methods of producing CNTs will then be reviewed, followed by existing processes that utilize waste plastics as carbon feedstocks for their production. At the end of this review, challenges faced by upcycling process and suggested solutions will be discussed.

1.1.4 Carbon Nanotubes: Synthesis, Properties, and Applications

CNTs consist of coaxial tubular graphene sheets, with lengths in the order of micrometers (1 × 10^{-6} m) and diameters in the order of nanometers (1 × 10^{-9} m).[50, 51] Carbon nanotubes (CNTs) have been studied for more than 20 years since being reported by Iijima.[52-54] The appealing properties of CNT fall essentially in four categories: (i) Electrical: semiconducting or metallic behavior, 100 times more conductive than copper.[55, 56] (ii) Mechanical: very high tensile strength (100 times higher than steel).[57-62] (iii) Thermal: high thermal stability and thermal
conductivity.[57] (iv) Chemical: chemically inert while affinitive with chemical/biological functional groups.[63-65] (v) Structure: ideal one-dimensional (1D) system with anisotropic properties, with extremely high aspect ratios.[66-68] Potential applications of nanotubes nowadays have become overwhelmingly widespread,[47, 69-72] examples of which include but are not limited to composites,[73-78] electrodes,[79-84] electronics,[85-92] photovoltaic devices,[93, 94] biological (Table 3).[95, 96]

Figure 4: Suggested relations between the CNT production capacity (ton/year) and predicted unit price ($/kg). Reprinted from Ref. 73, with permission from Wiley.

Entering into the growth phase of product life cycle,[47, 72] increasing usage of CNTs in commercial products is part of the beginning of the nanotechnological revolution. The global CNT production capacity in 2011 was estimated to be larger than 4500 tons,[47] and the production capacity is projected to be over 14,000 tons by 2016 at a compound annual growth-
Table 3: Potential Applications of Carbon Nanotubes

<table>
<thead>
<tr>
<th></th>
<th>Large-volume applications</th>
<th>Limited-volume applications (mostly based on engineered nanotube structures)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Present</strong></td>
<td>– Battery electrode additives (MWNT)</td>
<td>– Scanning probe tips (MWNT)</td>
</tr>
<tr>
<td></td>
<td>– Composites (sporting goods; MWNT)</td>
<td>– Specialized medical appliances</td>
</tr>
<tr>
<td></td>
<td>– Composites (electrostatic discharge applications; MWNT)</td>
<td>(catheters) (MWNT)</td>
</tr>
<tr>
<td><strong>Near term (less than ten years)</strong></td>
<td>– Battery and supercapacitor electrodes</td>
<td>– Single-tip electron guns</td>
</tr>
<tr>
<td></td>
<td>– Multifunctional composites (3D, damping)</td>
<td>– Multi-tip array X-ray sources</td>
</tr>
<tr>
<td></td>
<td>– Fuel-cell electrodes (catalyst support)</td>
<td>– Probe array test systems</td>
</tr>
<tr>
<td></td>
<td>– Transparent conducting films</td>
<td>– CNT brush contacts</td>
</tr>
<tr>
<td></td>
<td>– Field emission displays / lighting – CNT-based inks for printing</td>
<td>– CNT sensor devices</td>
</tr>
<tr>
<td></td>
<td>– CNT brush contacts</td>
<td>– Electromechanical memory device</td>
</tr>
<tr>
<td></td>
<td></td>
<td>– Thermal-management systems</td>
</tr>
<tr>
<td><strong>Long term (beyond ten years)</strong></td>
<td>– Power transmission cables</td>
<td>– Nanoelectronics (FET, interconnects)</td>
</tr>
<tr>
<td></td>
<td>– Structural composites (aerospace and automobile, etc.)</td>
<td>– Flexible electronics</td>
</tr>
<tr>
<td></td>
<td>– CNT in photovoltaic devices</td>
<td>– CNT-based biosensors</td>
</tr>
<tr>
<td></td>
<td></td>
<td>– CNT filtration/separation membranes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>– Drug-delivery systems</td>
</tr>
</tbody>
</table>
rate (CAGR) of 30.6%. Their revenues totaled $192 million in 2011 and are projected to grow over the next five years at CAGR of 22.4%, reaching $527 million by 2016. Expanding markets for CNTs' large volume applications place ever-increasing demands on lowering their production costs to the level acceptable by the end-user applications. It is estimated (in Figure 4) that the mass application of CNTs will be facilitated only when the price of CNTs approaches that of conductive carbon black.

CNTs are formed under appropriate conditions at the presence of carbonaceous feedstock, heat and, typically, catalysts. There are four major different methods for the production of CNTs: arc discharge, laser ablation, chemical vapor deposition (CVD), and combustion (flame) synthesis. After the discovery of multiwall and then single-wall carbon nanotubes by carbon vaporization in electric arcs, several varieties of this technique such as metal doping, different configurations of the electrodes or different types of carbon sources have been described. Synthesis of improved-quality single-wall carbon nanotubes have been reported using rather expensive laser irradiation of metal-doped carbon targets. Both methods can provide high quality CNTs; however, their yields are limited, mostly due to the available dimensions of the reactors and high energy consumption. The generation of well-aligned and uniform mats of multiwall as well as single-wall nanotubes, by chemical vapor deposition (CVD), i.e., growing materials from pyrolyzing hydrocarbons to the gas phase and depositing them onto solid surfaces, has been demonstrated. Additional technologies, such as plasma and microwaves, have been utilized to facilitate the CVD growth. The need for continuous external heating, which consumes large amounts of electric power, is a serious drawback for CVD's use
on an industrial scale (e.g., in a fluidized bed reactor[109-117]) for all but the highest end-value applications.[118-120] Another drawback of CVD is that most experiments reported require the injection of H$_2$, a highly flammable gas, to promote the reduction conditions needed to synthesize nanotubes.

Carbon nanotubes have also been generated by combustion synthesis. Compared with CVD pyrolysis, combustion synthesis has the advantage of being an exothermic process, i.e., not external heating (i.e., consumption of electricity) is needed. Carbon donors such as carbon monoxide or small hydrocarbons are generated in situ by means of a combustion process while a catalyst (either fixed or floating) is introduced, in a fashion similar to the above-described CVD techniques. The use of suitable combustion equipment and precise settings of operating conditions such as fuel/oxygen ratio, dilution with inert gas, fresh gas velocity, and pressure allows for accurate control of the CNT-forming process. Sufficient understanding of the correlations of the parameter space characterizing the nanotubes is expected to lead to a large-scale and high-yield production process of carbon nanotubes with well-defined and homogeneous properties.[121-123] Formation of multiwall carbon nanotubes by immersion of metallic substrates in methane-and ethylene-fueled, co-flow diffusion flames,[124-136] and of single-wall nanotubes by addition of metalloccenes to the fuel-stream of acetylene- or ethylene diffusion flames has been reported.[124] Multiwall carbon nanotubes were also observed in opposed-flow methane-oxygen diffusion flame with and without immersion of metal catalysts.[137-139] CNTs of different morphologies can be selectively produced with premixed flames of fuels having dissimilar chemical structures.[140] Small amounts of single-wall carbon
nanotubes (SWCNT) were identified in the condensed matter of partially premixed sooting acetylene and ethylene flames in which metalloccenes (Fe(C₅H₅)₂ and Ni(C₅H₅)₂) were vaporized and added to the flame-feed;[141] whereas multiwall carbon nanotubes (MWCNT) were observed in corresponding benzene flame. Commercially, large-scale production of SWCNTs of good quality has been achieved by using natural gas or methane as fuels.[142] In-line filtration allowing for continuous operation of SWCNT and product recovery was implemented using commercial metallic cartridges.[143, 144]

Current technologies for large-scale production of CNTs (either CVD or combustion synthesis) require intensive consumption of premium feedstocks, such as methane,[145, 146] ethylene,[147, 148] carbon monoxide (CO),[149-151] and hydrogen (H₂).[150] Therefore using waste plastics as inexpensive feedstocks can contribute to the cost reduction of CNT production, which may accelerate CNTs large-scale use in consumer/industrial products. This will in turn further stimulate the utilization of post-consumer waste plastics.

1.2 Waste Plastics as Low Cost Feedstocks for CNT Growth

The concept of synthesizing CNTs using solid polymers was first reported about 16 years ago.[152-155] Since then there have been numerous efforts on further advancing such low cost CNT synthesis route. Work have been done with regards to types of plastics, conversion processes, growth conditions, catalysts, and quantities and qualities of the resulting CNTs. Various processes have also been explored for such conversions, and there is one (and the only one up-to-date) review article covering this topic.[156] Nevertheless, that work examined
processes based on the reactors types alone (autoclave, crucible, fix bed (tube furnace, muffle furnace), moving bed, fluidized bed, etc.). Instead, the authors hereby focus on both the common and on the differentiating features of the existing waste-plastics-to-CNT conversion processes. Thereby, such conversions may be classified into two categories: (1) one-pot conversion where synthesis of CNTs occurs upon the in situ formation of carbon feedstocks from the solid plastic waste; and (2) stepwise conversion where synthesis of CNTs occurs after the formation of carbon feedstocks from the solid plastic waste. Typical processes are summarized in Table 4, which includes their representative CNT products, related conversion conditions, as well as corresponding references.

Table 4: Summary of Representative Waste-to-CNT Conversion Processes

<table>
<thead>
<tr>
<th>Representative CNT products (taken by scanning electron microscopy)</th>
<th>Polymer feedstock</th>
<th>Catalyst/Temperature/Synthesis duration</th>
<th>Process description</th>
<th>Research groups, references / permission</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Image of CNTs]</td>
<td>• PE + ferrocene + MAPP/ 700°C /12 hrs</td>
<td>• Plastics mixed with catalysts in an autoclave, heated by electronic furnace, leading to simultaneous plastic decomposition and CNT formation</td>
<td>Kong and Zhan(^{158}) Reproduced from (^{158}), with permission from Elsevier.</td>
<td></td>
</tr>
<tr>
<td>Image</td>
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| ![Image](image86x564to263x708.png) | **b** | **PP + Ni2O3 + OMMT + MAPP / 830°C / unknown duration**<br>Plastics mixed with catalysts in a crucible, heated by flame, leading to simultaneous plastic decomposition and CNT formation | Tang and co-workers\textsuperscript{159}
Reproduced from \textsuperscript{[159]}, with permission from Elsevier. |
| ![Image](image85x403to263x547.png) | **c** | **PP/PE/PET + quartz-rich sand or alumina particles / 450-850 °C / unknown duration**<br>Plastics mixed with catalysts within a fluidized bed, heated by electronic furnace, leading to simultaneous plastic decomposition and CNT formation | Arena and Mastellone\textsuperscript{160}
Reproduced from \textsuperscript{[160]}, with permission from Elsevier. |
<p>| <img src="image86x221to264x365.png" alt="Image" /> | <strong>d</strong> | <strong>PE + stainless steel meshes / 800 °C / 1 minute</strong>&lt;br&gt;Plastics were first pyrolyzed in quartz tube, the resulting gaseous carbon feedstock were then channeled into a separated reactor where located the catalysts, both heated by electronic furnaces, leading to sequential plastic decomposition and CNT formation | Zhuo, Levendis and co-workers |</p>
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1.2.1 One-Pot Conversion of Plastics into CNTs

One-pot synthesis of carbon nanotubes typically starts with solid polymers which are mixed with catalysts. A heat resource is then applied to catalytically decompose (pyrolyze) the plastics. The
decomposed products, either in liquid or gaseous phases, serve as carbon sources for the growth of CNTs on the catalysts. Polymers, such as polyethylene (PE),[157-161] polypropylene (PP),[160, 162-168] polystyrene (PS),[163] polyvinyl alcohol (PVA),[169] polyvinyl chloride (PVC),[170] polytetrafluoroethylene (PTFE),[171] polycarbosilane (PCS),[172] phenol formaldehyde (PF),[173] and polyethylene terephthalate (PET),[164] etc. have been studied using this method (Table 4). Various catalysts have been examined, including transition metals in either elemental form (nickel,[157, 174, 175] iron,[163, 172] etc) or in chemical compound form (nickel oxides,[168, 176-178] ferrocene,[158, 167] ferrous chloride,[171] cobalt acetate,[159] etc.) among others. Heat is supplied by either electric furnaces (fixed beds,[163, 178, 179] autoclaves,[175] and fluidized beds,[160, 164]), or by combustion of fuels.[162, 166, 168, 177, 180] This one-pot synthesis features simultaneous plastic degradation and the CNT synthesis, and efforts have been made to reveal how it proceeds. Jiang et al. proposed a possible reaction mechanism, using PP as the sample feedstock[166] with nickel-based catalysts, as illustrated in Table 4. With the presence of catalysts, plastics are degraded (decomposed), by active intermediates of carbenium ions, but not free radicals which play a major role in noncatalytic thermal decomposition of plastics. It is suggested that the resulting “free carbons” from catalytic pyrolysis of plastics will then dissolve into the catalyst, diffuse through and then precipitate at its surface to form CNTs. Such one-pot synthesis can be greatly affected by utilizing a combination of metal catalysts with solid acids (such as organically-modified montmorillonite (OMMT)[166, 168] or zeolite[177]), chlorinated compounds (such as CuCl),[180] and/or activated carbon.[181]
Solid acids are suggested to provide the intermediate proton acidic sites, which will assist breaking down the molecular chains of the plastics[166, 182] favoring the formation of CNTs. On the other hand, chlorine radicals could promote the dehydrogenation and aromatization during the degradation of the plastics,[183] resulting in more carbon nanofiber and less CNTs.[180] Activated carbon plays multiple roles in the conversion of plastics into CNTs,[181] such as (1) to absorb and to be functionalized by the fragment radicals from the plastics decomposition products, (2) to promote the formation of light hydrocarbons and aromatic compounds (especially the diaromatic and polycyclic hydrocarbons) through the fragment radicals as well as the aromatic intermediates, and (3) to further assist catalyzing the dehydrogenation and aromatization of the aromatic intermediate or PAHs.

Different reaction conditions (temperatures, catalyst compositions/concentrations/loads, reaction durations, etc.) usually lead to CNTs with various quantities and qualities. In addition to existing reviews on such topics,[156] the authors would like to briefly discuss the one of the features this one-pot synthesis processes: the CNT production yield. It is worth mentioning, that there are at least three different definitions in production yield: the mass production rate of CNTs (unit: g/h), the mass of CNTs over the mass of the catalyst (unit: g/g), and the mass of CNTs over the mass of the feedstock (unit: g/g or %). The former two definitions are commonly used in traditional CNT production processes, as the corresponding focuses are either on the end products (CNTs) or on the activities of the catalysts. In waste-to-CNT conversion processes, however, the third definition is predominately used, as the focus of such processes is on conversion efficiency. That is why the data compiled from all different processes is not directly comparable. The yield could
be as low as several percent (e.g. 5% in Ref. 178), and this number can reach 50% or higher,[156, 178] under optimum conditions. Such a high yield conversion is achieved typically in a setting where the mix of plastics and catalysts is enclosed within a container, such as a crucible. Comparing with an open system such as in a quartz tube reactor, where the pyrolyzed products (usually in gaseous phase) are carried away by the processing gas, this enclosed environment enables a longer reaction time between the plastics pyrolyzates and the catalysts. Therefore this could be a reason for such high conversion rate. High temperatures (>700°C) and compound-based catalysts are also found to lead to high CNT yields.[158, 178]

The impurities in the CNTs generated by both one-pot processes and stepwise processes usually consist of residual catalysts and amorphous carbon. Impurities typically account for 10 wt % of the as-produced CNTs. The lowest amount of impurity reported was 0.3 wt %[178] as determined by thermogravimetric analysis (TGA), a common method to investigate the impurity and thermal stability of CNTs. In order to keep the number of impurities low, efforts should be made to optimize process parameters as: the components and dispersion of catalysts, the feeding rates of plastics, the reaction temperature, etc., for the catalysts be kept active and produce CNTs with minimum defects.

### 1.2.2 Stepwise Conversion of Plastics into CNTs

The stepwise conversion process features sequential reactions, typically starting with the thermal decomposition of plastics. As a second step, the resulting gaseous products (hydrocarbons) are then channeled downstream where they react with catalysts to form CNTs.[184] This is the method applied in the first reported explorations of plastics to CNT conversion,[153-155] since
then additional works have been done to investigate the underlying fundamentals as well as to advance the technology of such conversion processes. The plastics-to-CNTs conversion mechanism is rather complicated, as it combines the steps of high temperature plastic cracking,[185, 186] high temperature oxidation/combustion,[187, 188] thin film formation through chemical vapor deposition and gas-solid chemical conversion through heterogeneous catalysis.[50, 189, 190] A comprehensive review has been done by Bazargan and McKay, addressing among other topics this formation mechanism,[156] whereas this concise review highlights significant technology developments.

An inherent feature of such a stepwise process is that it enables individual controls over its subprocesses. That is to say, decomposition (pyrolysis) of plastics can be processed without interference with the synthesis of CNTs. For instance, Yang et al. employed a three-stage reactor, where catalysts (ferrocene) was first sublimated, in the first reactor, before entering the second reactor, where plastics (either PE, PP, or PVC) were decomposed.[191] The mixture of the formed catalysts and the gaseous pyrolyzates was then channeled into the third reactor, where CNTs were formed and collected. Their setting enabled independent controls of reaction temperatures (120–140°C for ferrocene sublimation, 450°C for plastics decomposition, and 800–850°C for CNT growth). With reaction time in the order of 10 min, lengths of CNTs were typically in the order of 100 μm. It is not clear, however, whether the iron particles (sublimation products of ferrocene) only catalyzed the growth of CNTs, or they also participated in the thermal decomposition/pyrolysis of plastics.
An improved two-stage stepwise process was investigated by Liu et al.[192] Polypropylene (PP) was catalytically pyrolyzed over HZSM-5 zeolite in a screw kiln reactor, and the resulting pyrolysis gases were subsequently decomposed over nickel catalysts in a moving-bed reactor. CNTs and hydrogen were produced simultaneously, and it was found that 700°C was the optimum decomposition temperature, in terms of maximum productions of both CNTs and hydrogen with a synthesis temperature of 750°C. Similar work was reported by Wu et al., where a fixed-bed two-stage reaction system was used.[193] Waste plastics samples were pyrolysed in N2 in the first stage at 500°C, and the resulting compounds were further used to synthesize CNTs at 800°C in N2. Water was injected into the second reactor, where catalysts (Ni/Ca-Al or Ni/Zn-Al) were also present, to jointly facilitate the CNT formation.

Recently, the authors developed a hybrid reactor, combining sequential feeding, pyrolysis, premixed-combustion, and CNT synthesis process. (Zhuo et al.[194-200]) To achieve conversion of solid hydrocarbon fuels to CNTs, quantities of a solid fuel, in pelletized form, were first thermally pyrolyzed into a stream of gaseous decomposition products (pyrolyzates) inside a pyrolyzer furnace at 600 to 800°C, depicted on the left side of Figure 5. Pyrolysis occurred in inert nitrogen, to prevent the ignition and combustion of the pyrolyzates therein. The pyrolyzates then flowed through a mixing venturi where they were thoroughly mixed with preheated oxygen-containing gases. The oxygen/pyrolyzate
Figure 5: a: Four-stage laminar-flow, electrically-heated, muffle furnace, used for proposed work; zone 1: steady-state, steady flow, continuous feeding stage, zone 2: pyrolysis stage, zone 3: combustion stage*, and zone 4: CVD-synthesis stage. b: Ceramic (SiC) honeycomb filter manufactured by Ibiden. c: stacked catalyst in the forms of either woven screens or honeycomb structures. *: A flame is present at the combustion stage only when oxygen-containing gases are added to the venturi.

charge autoignited at the exit of the venturi, forming a premixed flame. The fuel/oxygen ratio in the venturi was set to be fuel-rich (i.e., oxygen deficient) by adjusting the amount of oxygen introduced to the venturi. This ensured that there were large amounts of carbon-bearing compounds (CO and unburned aliphatic hydrocarbons), hydrogen, and water vapor in the combustion effluent, as needed for the efficient growth of CNTs. The combustion effluent then entered the second furnace where fixed catalyst substrates were also preinserted (such as stainless steel screens or honeycombs). Growth of CNTs occurred on the catalyst substrates at 600 to 1000°C. To prevent soot, which may be generated in the flame, from entering the second furnace and inadvertently depositing on the catalyst substrates and contaminating them, a high-temperature ceramic barrier filter had been inserted at the entrance of the CVD synthesis chamber, see Figure 5. This feature allowed operation of the apparatus above and beyond the
equivalence ratio \( \phi(\text{defined as } \frac{m_{\text{fuel}}}{m_{\text{oxygen}}}_{\text{actual}}/ \frac{m_{\text{fuel}}}{m_{\text{oxygen}}}_{\text{stoichiometric}}) \) that corresponds to the soot onset thresholds.\[140, 201\] The ceramic filter may be periodically thermally regenerated in situ, at 1000°C in air, to burn any entrained soot particles.

Another unique feature lies on the design of the venturi section, which enables the introduction of additional materials, such as one or more gases (e.g., oxidizing agents such as oxygen gas, chlorine gas, carbon dioxide, any other gas containing oxygen, and the like), or catalysts (such as ferrocene) to mix with the gaseous decomposition products, which enter the venturi section.

Use of stacked catalyst substrates (screens or honeycombs) will allow not only for high-yield production of CNTs but, also, for selective and detectable depletion of some carbon-bearing gases in the combustion effluents as CNTs form. Sampling the gases before and after the catalyst substrates from sampling ports 1 and 2, as illustrated in Figure 5, can help determine which gases are likely growth agents for CNTs. In summary, this process incorporates the following unique features: (a) It pyrolyzes or gasifies solid wastes to generate gaseous carbon-bearing components. (b) It affords control of the fuel-to-air ratio in the venturi from fuel-lean to fuel-rich and, to the limit, to purely pyrolytic conditions at the absence of oxygen. (c) The pyrolysis and the CNM synthesis occur in two separated stages, which afford individual control of the subprocess conditions. (d) The risks of handling highly reactive gases (such as H2), and/or highly toxic gases (such as CO), are eliminated as they are generated in situ in an inert gas. Finally, (e) this process can generate a hydrogen-enriched syngas.
Moreover, this process can be designed to be energy efficient.[194] For instance, Jinno et al.[202] measured the heat of pyrolysis of polyethylene (PE) to be 254 kJ/kg, independently of the heating rate. Comparing this heat of pyrolysis with the heating value (energy content) of this polymer, which is 46,000 kJ/kg,[203] it becomes evident that a small fraction of the heat released during combustion may be fed back and pyrolyze this solid fuel. Similarly, the energy fluxes necessary to pyrolyze polypropylene (PP) and polystyrene (PS) are 423 and 1,499 kJ/kg, respectively.[202] Thus, the energy balance of the proposed process is overwhelmingly positive. A portion of the heat released during the combustion of the polymer pyrolyzates may be fed back to the pyrolyzer through a heat exchanger to gasify incoming precursors, whereas the remaining heat may be used elsewhere as process-heat or to generate electricity. Regarding the environmental impact of this process, it should be stated that the use of premixed flames, high temperature filtration, and possibly a post-process afterburner can drastically reduce unburned or partially burned health-hazardous species, as shown before in the author's laboratory.[204-210] The generation of the greenhouse gas CO$_2$ could be an issue when waste polymers are used as feedstocks. However, by using such waste hydrocarbon-based post-consumer products, the conventionally used, more valuable premium hydrocarbons are merely substituted, and thus, CO$_2$ emissions (that would have been released during their extraction and processing) are avoided. In addition, there are also benefits to cleaning the earth of nonbiodegradable wastes. Generating value-added products, such as CNMs, from recycled waste plastics is thought to enhance the motivation for recycling, lower the cost of the products, and in turn, help overcome the hurdles of their large-scale use in consumer and industrial applications.
1.2.3 Challenges and Possible Solutions

One of the major challenges in plastic-wastes-to-CNT up-cycling comes from the nature of waste feedstocks, where there is a lack of consistent and reproducible supply of carbon feedstock with controlled quality (in terms of compositions and impurities). Feedstocks from recycling streams are typically mixtures of various types of plastics.[19] The resulting pyrolysis products, of different compositions, are known to affect the formed CNTs, while the detail correlations are yet to be revealed. What is more, waste plastics containing fillers and/or other additives could have detrimental effects on the quality of formed CNTs.[211] These two problems get further complicated when there are variances among different batches of waste plastic streams.

Another challenge of such up-cycling processes lies on the process complexity. Comprehensive scientific investigations are still needed in both one-pot and stepwise methods, especially those involved on the driving force behind the proposed waste-to-CNT up-cycling process. In the case of stepwise method, for instance, whereas gaseous feedstocks have been correlated directly to CNT products,[212-216] the fact that these feedstocks pyrolyze at the high reaction temperatures therein (>400°C) to form intermediate products has been largely ignored.[217-219] Therefore, the CNT catalysts therein have experienced a blend of carbon-bearing gases, which are very different from the input feedstocks. Hence, it remains unresolved whether the CNT synthesis process consumes the carbon-bearing gases equally or selectively.[194, 195] Simply building a connection between the initial feedstocks and the CNT products is not sufficient. The thermally-driven chemistry that takes place between the input and the output also needs to be accounted for.

It is therefore worth examining what carbon-bearing gases get consumed at the catalyst
substrates, and are thereby converted to CNTs. Further understanding of the detail reaction schemes will help engineers control the quality of produced CNTs that will satisfy the commercialization objectives.

There are solutions to overcome such challenges, albeit empirically, by adapting technology advancements from plastic waste recycling processes, as well as from CNT synthesis processes. For example, intelligent waste identification/separations can be assisted by (tribo)electrostatics, laser-induced plasma spectroscopy,[220, 221] laser-induced breakdown spectroscopy,[222-224] density media,[225] artificial neural networks,[226] etc. Plastic waste decompositions, on the other hand, can be benefited from the well-established pyrolysis/gasification fundamentals,[227-233] reaction chemistry (thermodynamics,[234] kinetics,[235-238] mechanisms,[237] etc.), as well as the related technology developments, such as those of catalysts,[239-241] additives,[242, 243] process,[244] or their combinations. Last but not least, CNTs synthesis, especially their yields with controlled quality, could also gain from recent progresses in process engineering at nanoscale.[21, 111, 245-249]

1.3 Conclusions

In summary, upcycling plastics waste into high value CNTs is indeed a sustainable solution with a promising future as it allows for conversion of post-consumer products to value-added products and can help alleviate the burden of solid wastes on the environment. Its realization from concept is highly multidisciplinary. Partnerships among fundamental science, engineering development, etc. are essential for integrating such process with existing manufacturing methods.[47]
Knowledge and experience from industry on existing facilities, such as those for recycling, gasification/pyrolysis, as well as those of fluid catalytic cracking and hydrocracking plants, can be instrumental.

1.4 Acknowledgments

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1.5 Biographies

Chuanwei Zhuo received his M.S in Mechanical Engineering from Northeastern University, USA, where he is now a PhD candidate, and his B.S. with 1st-grade distinction in Thermal Energy and Power Engineering from Harbin Institute of Technology, China. His research interests lie in waste hydrocarbons up-cycling, energy and fuel conversion, synthesis and characterization of carbon nanomaterials, as well as the their applications in transportation, fire safety, and environmental remediation.

Yiannis Levendis received his Ph.D. from California Institute of Technology in Environmental Engineering Science, and M.S. and B.S. from University of Michigan in Mechanical Engineering. He is now a College of Engineering Distinguished Professor at Northeastern University. His research interests lie in alternative fuels, clean coal, energy conversion, combustion science and
engineering, and atmospheric pollution. He is a fellow of SAE and a fellow of ASME, and a recipient of George Westinghouse Gold Medal awarded by ASME.

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CHAPTER TWO

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87
2. Synthesis of Carbon Nanotubes by Sequential Pyrolysis and Combustion of Polyethylene

Abstract

Carbon nanotubes (CNTs) were synthesized from polyethylene using a pyrolysis–combustion technique. Pre- or post-consumer polyethylene (in strips, pellets or ground particles) was pyrolyzed to gaseous products, which were then combined with an oxygen-containing gas and auto-ignited to create a fuel-rich flame. The combustion effluent was used to synthesize multi-wall CNTs using stainless-steel wire mesh as both catalyst and substrate. An overall CNT yield in the order of 10%, by mass relative to the initial carbon in the fuel, was typically achieved before purification. The viability of partial conversion of a readily-available waste stream to the value-added product of CNTs was demonstrated, combining the economy and process safety aspects of flame synthesis with the control of synthesis temperature that chemical vapor deposition methods typically afford.
2.1 Introduction

As production of CNTs moves from laboratory-scale to industrial-scale, their worldwide market is expected to grow from $215 million in 2009 to over $9 billion by 2020.\(^1\) Industrialscale production of both single-walled and multi-walled carbon nanotubes (SWCNTs and MWCNTs) is currently achieved through energy- and resource-intensive processes, such as chemical vapor deposition (CVD) or flame synthesis (pertinent references in italics). Carbon sources of various kinds have been used as feedstocks, and past research has targeted mass production [1–6], to match the needs of industrial applications with specific fabrications, such as diameter selected synthesis [7], and length controlled synthesis [8,9]. In both CVD and flame synthesis processes, carbon feedstocks have been carbon monoxide (CO) [8,10], carbon dioxide (CO\(_2\)) [11,12], hydrocarbons or hydrocarbon-contained organo-metallic precursors [13–15]. Hydrocarbons, such as methane [16,17,18], ethyne (acetylene) [5,19,20–22], ethylene [4,22,23], ethane [22,24], propane [22,25], ethanol (alcohol) [26,27,28], acetone [29], benzene [30–32], toluene [33], as well as some C12 and C16 hydrocarbon templates (alkyl chains) [7] have been confirmed as carbon sources of CNT synthesis. Compared to CVD synthesis, combustion synthesis has the advantage of being an exothermic process. Carbon feedstocks such as CO and light volatile hydrocarbons can be generated in situ by means of a combustion process, and catalytic growth of CNTs can be achieved in a fashion similar to CVD techniques. The use of suitable combustion

equipment and implementation of appropriate operating conditions, such as fuel/oxygen ratio, dilution with inert gas, input gas velocity and operating pressure, allows for control of the CNT-forming process.

Both CVD and flame synthesis technologies consume costly premium hydrocarbons as well as highly-flammable chemicals, such as hydrogen (H₂). Thus, for industrial CNT manufacturing processes to become sustainable and inherently safe [14], it would be sensible to use readily-available alternative fuels, such as existing waste streams. Plastics, in which carbon is the major constituent, are a rapidly-growing segment of municipal solid waste streams. Currently, 30 million tons of post-consumer plastics are generated every year in the US alone, representing 12 wt% of the total municipal waste stream [15]. Their pyrolytic conversion to valuable gaseous fuels has been previously demonstrated. For instance, nearly quantitative decomposition of high-and low-density polyethylene (HDPE and LDPE), representing 60 wt% of the overall municipal and industrial waste-plastics streams, to its monomer precursor ethylene and other gaseous hydrocarbon species has been shown in this laboratory and elsewhere [16–18].

Efforts have been made elsewhere to utilize the polymeric materials as carbon feedstock for the synthesis of CNTs [34–38]. For example, Kiselev et al. [34] used the gaseous pyrolyzates of polyethylene for CNT synthesis; Jiang et al. [36] mixed melted polypropylene with a catalyst, and then heated the mixture to a temperature of 830 °C to obtain CNTs. More recently, Pol and Thiyagarajan [38] combined pieces of HDPE or LDPE with a cobalt acetate catalyst, heated the mix to 700°C and baked it at that temperature for 2 h. Above 600 °C, chemical bonds in the
polymer broke down and MWCNTs grew on the surface of the catalytic particles through solid-solid phase transformations.

A hybrid flame/CVD process was developed in this laboratory to synthesize CNTs from waste fuels. While correlations between synthesis conditions and detailed characteristics of the produced CNTs are being established, CNTs cover a range of hollow structures with high aspect (i.e., length-to-diameter) ratio. Wall structures are graphene-based (i.e., MWCNTs), and graphene stacks span from nearly well parallel to less organised configurations. This hybrid flame/CVD process takes advantage of the low enthalpy needed for thermal decomposition (pyrolysis) of plastics to gaseous hydrocarbon products (a small fraction of the enthalpy of combustion [39]). To generate such light hydrocarbons (LHCs), plastics are thermally pyrolyzed to an overwhelmingly gaseous stream. Subsequently, the gaseous pyrolyzates (LHCs and H₂) are then either directly-used as CNT feedstock, or are mixed with oxygen-containing gases and then burned to generate CNT feedstock of a different composition (LHCs, CO, CO₂, H₂, and H₂O). The generation of the feedstock gases and the synthesis of CNT occur in separate reactors, whose operational parameters can be controlled independently. This feature combines advantages of the flame synthesis and of the CVD synthesis of CNT, namely in situ generation of gaseous feedstock and good control of the synthesis temperature. Aside of providing low-cost feedstock for CNT growth, this process has also the potential of being energy-sufficient in the case where the polymer pyrolyzates are burned, and the (exothermic) enthalpy of combustion is successfully harnessed and used to support the pyrolysis and synthesis sub-processes. In a well-designed system, energy surplus may be even realized.
2.2 Experimental Apparatus, Materials and Procedures

The experimental setup consists of three stages: (a) a polymer pyrolysis, (b) mixing-venturi/burner and, (c) CNT synthesis, see Fig. 6. Electrically-heated furnaces were used, fitted with quartz tubes. The following polymers were used: HDPE and LDPE powders, from Sigma–Aldrich, 0.25–0.3 mm; HDPE and LDPE virgin pellets, 3–4 mm; shredded post-consumer HDPE bottles, shown in Fig. 6b. Samples of these materials were loaded in a porcelain boat and were inserted into the purged and preheated pyrolyzer section of furnace. Nitrogen served as the inert carrier gas ensuring that non-oxidizing conditions prevailed in the pyrolyzer. Samples of the pyrolysis gas were withdrawn with syringes, mounted on a syringe pump; they were analyzed by gas chromatography (Agilent GC 6890A), using flame-ionization and thermal conductivity detectors (FID and TCD). The pyrolyzate gases passed into the venturi (8mm ID), see Fig. 6, where they were mixed thoroughly with either air or oxygen-enriched air. The efficiency of mixing in the venturi has been confirmed in previous work [40–45]. Upon auto-ignition and formation of a premixed flame, CNT precursors such as CO, CO₂ and pyro-synthesized hydrocarbons were generated. Conditions were kept exceedingly fuel-rich, i.e., \( \phi > 2 \), to maximize the concentration of the CNT precursors.

The combustion gases were channeled into the third stage of the apparatus where catalyst screens were placed perpendicularly to the flow and were maintained at a predetermined synthesis

\[ \text{Equivalence ratio is defined as: } \phi = \frac{(m_{\text{fuel}}/m_{\text{oxygen}})_{\text{actual}}}{(m_{\text{fuel}}/m_{\text{oxygen}})_{\text{stoichiometric}}} \]
temperature ($T_{\text{synthesis}} = 750$ °C). Because combustion of each batch of polymer (1 g) lasted for roughly 30 s, CNT synthesis also lasted for 30 s. Despite batch operation, a fairly steady flame was established during each combustion run. Since in these experiments the sooting thresholds for ethylene [46] were exceeded, partially because of the transient (batch) combustion of the polymer, the formation of some soot could not be precluded. Hence, to prevent catalyst deactivation by deposition of soot formed in the flame, a high-temperature silicon carbide (SiC) honeycomb barrier filter (Ibiden Corp.) was placed inside the quartz tube, between the flame and the catalyst, see Fig. 6. This filter has a retention efficiency of 97% for soot particles bigger than 1 lm [47,48]; it was periodically thermally-regenerated by passing high-temperature air.

Figure 6: (a) Three-stage laminar-flow, electrically-heated, muffle furnace, used for the CNT synthesis; zone 1: pyrolysis stage, zone 2: combustion stage*, and zone 3: synthesis stage. (b) Post-consumer plastic bottles (made of HDPE) used as carbon feedstock, and (c) ceramic (SiC)
honeycomb filter manufactured by Ibiden. (*) A flame was present within the combustion stage only when oxygen was added to the venturi.

While particulate soot was captured and sequestered within the ceramic filter, the gaseous combustion products entered the preheated third stage of the apparatus, where they interfaced with the metal catalyst surface. For this purpose, small screens (6.5 cm$^2$) of 304 stainless steel (157 wire/cm mesh with 0.002 cm diameter wire) were used as catalysts either as received, or stainless-steel coated with additional catalyst. Either cobalt (Co) or nickel (Ni) catalysts were applied to the screens, in 4 nm thick films, by means of physical vapor deposition (PVD).

The interaction between the catalysts and carbon-bearing gases generated CNT on the surface of the substrates. Hydrogen and water, byproducts of the combustion of PE pyrolyzates, were expected to moderate the rate of carbon deposition and prevent catalyst deactivation and poisoning, by continuous surface cleaning [49]. The major species present at the exit of the synthesis furnace were determined using GC coupled to FID and TCD.

Upon completion of the reactions, as indicated by the extinction of the visible flame, oxygen was turned off immediately to avoid any oxidation of the material grown on the screens. The catalysts were then allowed to cool-down in the reactor, in a stream of nitrogen, until the temperature therein dropped below 200 °C. The screens were then removed and prepared for analysis by scanning and transmission electron microscopy (SEM and TEM), and other techniques.

SEM analysis was conducted with a Hitachi 4800 instrument using a voltage of 3 kV and a working distance of 8.2 mm. Substrates removed from the reactor were placed directly on the SEM imaging stage. For TEM, a JEOL 1010 microscope was used with an accelerating voltage
of 70 kV, and a JEOL 2010 instrument was operated with an accelerating voltage of 200 kV. To remove CNTs from the substrates for further characterization, the screen meshes were immersed in ethanol, which was then sonicated until the solution turned from transparent to black. As it is often difficult to remove CNTs from their substrates (see Tribolet and Kiwi-Minsker [50]), the ethanol solution was replaced often until it did not darken any more. Upon removal of the CNTs, the meshes were examined using SEM, and there was no evidence of CNTs. Drops of the resulting dispersion were deposited on a holey carbon film (200 copper mesh, EMS, Hatfield, PA) which was then inserted in the specimen chamber of the TEM instrument. For thermogravimetric analysis (TGA) measurement, material grown on metal screens was removed by sonication in ethanol, followed by evaporation of the ethanol. The resulting powder was analyzed under air using a TGA i1000 instrument (Instrument Specialists, Twin Lakes, WI), using a heating rate of 5 °C/min. Elemental analysis was performed using energy dispersive X-ray spectroscopy (EDS). Signal were collected for 60 s and processed by means of INCA software. Brunauer–Emmett–Teller (BET) surface area measurements were conducted by Clear Science Inc. (Minneapolis, MN), using a Micromeritics Gemini 2375 Surface Area Analyzer and nitrogen as adsorbate gas. X-ray diffraction (XRD) analysis was carried out using a Rigaku 185mm Bragg Brettano Diffractometer.
2.3 Experimental Results

![SEM images of CNTs generated by combustion of post-consumer HDPE pyrolyzates at two different magnifications.](image)

Figure 7: Representative SEM images of CNT generated by combustion of post-consumer HDPE pyrolyzates at two different magnifications ($T_{\text{pyrolysis}} = 800 ^\circ \text{C}, T_{\text{synthesis}} = 750 ^\circ \text{C}, \text{O}_2$ mole fraction at the venturi was 50%, the substrate/catalyst was 304 stainless steel).

Upon completion of each experiment, the mesh substrates were covered with a layer of black material. SEM images, taken at different magnifications without any prior sample preparation, reveal the existence of tubular structures grown on the surface of the substrates (Fig. 7a and b). The CNTs illustrated here were generated by combustion of post-consumer HDPE pyrolyzates at $T_{\text{pyrolysis}} = 800 ^\circ \text{C}, T_{\text{synthesis}} = 750 ^\circ \text{C}$, with 50% $\text{O}_2$ mole fraction at the venturi; the substrate/catalyst was 304 stainless steel. In Fig. 7a, the valley-like ‘gap’ is actually the adjuccntion area between two interwoven wires of the substrate/catalyst screen, see also Fig. 9. Hence, CNTs were synthesized on all sides of the screen mesh wires. As shown in Fig. 8a and b, TEM images of the same samples prepared for SEM revealed tubular MWCNT structures with
lengths typically of 1–5 µm and diameters between 15 and 84 nm were identified. A statistical analysis of the representative MWCNT diameter with a sample size of 475 CNTs indicated a lognormal distribution with a mean tube diameter of 43.6 nm and one standard deviation (r) of 16.6 nm (Fig. 8c).

Examination of the wall structures showed the presence of parallel graphene layers (Fig. 8a and b). For instance, the CNT shown in Fig. 8b exhibited 16 graphene layers with a separation of about 0.36–0.38 nm. This inter-lattice distance is consistent with the value of 0.344 nm that has been previously calculated as the theoretical distance between graphene layers [24], and also reported based on measurements [25]. Wall defects, as seen with high-resolution TEM (Fig. 8b), may compromise the electrical conductivity and mechanical strength of CNTs. For instance, defects in the wall structures can cause energy concentration points and lead to premature failure [26,27]. Higher temperature and increased residence time are expected to reduce defects and to increase the degree of graphitization [51,52].
Figure 8: TEM image revealing a MWCNT with non-uniform diameter along the axis (a) and HRTEM image (b) with 16 layers of graphene; (c) representative lognormal distribution of MWCNTs; and (d) typical TGA analysis of MWCNTs. Post-consumer HDPE was used as feedstock ($T_{\text{pyrolysis}} = 800 \, ^{\circ}\text{C}$, $T_{\text{synthesis}} = 750 \, ^{\circ}\text{C}$, $O_2$ mole fraction at the venturi was 50%, the substrate/catalyst was 304 stainless steel).

The collected carbonaceous material was further assessed by TGA. As shown in Fig. 8d, a rather slow weight loss was evident until $\sim 450 \, ^{\circ}\text{C}$, thereafter a rapid decline was manifested until oxidation was completed at 600 $^{\circ}\text{C}$. Whereas the initial weight loss may be attributed to oxidation of tars, the consumption of material beyond 525 $^{\circ}\text{C}$ was consistent with the presence of MWCNT structures. The remaining residues, likely consisting of metallic compounds from the
substrate, have ranged from a few percent to about 20%. The high abundance of carbonaceous material is in agreement with SEM and TEM observations, as discussed above.

![Diagram of substrate/catalysts](image)

**Figure 9: Arrangement of substrate/catalysts used for measurable volume production of CNTs.** (a) Schematic of 25 parallel parallelstacked 304 stainless-steel meshes, 2 cm × 2 cm each; (b) SEM detail of the woven meshes where three-dimensional growth of CNTs occurred.

A BET surface area of 76.3 ± 0.9 m²/g was determined. In comparison to other nanostructured carbon materials as, e.g., SWCNTs [53], this is a rather small value. However, it may be of significant interest for Li storage in Li-ion batteries, since in those applications high surface areas lead to irreversible adsorption.

To obtain measurable yields of CNTs, 25 segments of substrate mesh, 4 cm² each, were placed normal to the flow direction, as shown in Fig. 9a. The cylindrical stainless-steel wires of each woven mesh provided a total surface area of 240 cm² for the synthesis of MWCNTs (Fig. 9b). In a typical single batch process which lasted for 30 s, a yield of 10% by mass relative to the initial carbon in the fuel was attainable before purification. This was sufficient for material characterization. A larger number of mesh segments can be utilized to further increase the yield.
EDS revealed the existence of nanoparticles at the tips of the CNTs, see Fig. 7b and the detail marked by an arrow in Fig. 13c. These particles consisted of nickel, iron, chromium, and manganese, showing that the catalyst particles have a heterogeneous composition as would be expected in a metal alloy, such as steel.

Additionally, the quality of the synthesized CNT was examined using Raman spectroscopy, and XRD (Fig. 10). Consistent with the strong G-band circa 1600 cm\(^{-1}\) of the Raman spectrum reflecting tangential oscillations [54], XRD reveals a significant degree of graphitization. However, the presence of the pronounced D-band around 1300 cm\(^{-1}\) is related to disordered carbon, i.e., defects and/or sp\(^3\) carbon.

![Figure 10: Baseline-corrected (a) Raman and (b) XRD spectra of CNT products. HDPE pellets were used as feedstock (T\(_{\text{pyrolysis}} = 800\) °C, T\(_{\text{synthesis}} = 750\) °C, O\(_2\) mole fraction at the venturi was 23%, the substrate/catalyst was 304 stainless steel).](image)

2.4 Results from a Parametric Study on Factors that Affect this Polymer-to-CNT Conversion Process

In order to assess the effects of the operating parameters of the process on the CNT products, parametric studies were conducted in terms of the temperature of the pyrolysis process, the oxygen concentration in the oxidizer gas introduced to the venturi, as well as the catalyst type for CNT synthesis. Key variables of the aforementioned parameters are summarized in Table 5. Particular emphasis was placed on (1) the identity of pyrolysis products (pyrolyzates), i.e., the gaseous fuels that were input to the combustion process; (2) the amount of oxygen that was input to the combustion process (this influences the composition of the combustion products that are feedstock to the CNT), and (3) the type and form of catalysts.

Table 5: Summation of the operational parameters.

<table>
<thead>
<tr>
<th>Pyrolysis temperature</th>
<th>650</th>
<th>Oxygen mole fraction at the venturi</th>
<th>0%</th>
<th>17%</th>
<th>21%</th>
<th>25%</th>
<th>Type 304 stainless steels with PVD coating</th>
<th>4nm nickel</th>
<th>4nm cobalt</th>
<th>304 stainless steels</th>
</tr>
</thead>
</table>
2.4.1 The Effect of Temperature of the Pyrolysis Process on the Yield of Pyrolyzates

Carbon-bearing gases, i.e., LHCs, CO, and CO₂, are thought to be carbon feedstock for CNTs [3,12,55], and are therefore a focal point of this work. It has been previously reported [56,57] that the yield of gas from pyrolysis of PE increases with temperature; it only accounts for 5.7 wt% at 500 °C, reaches a maximum of 96.5 wt% at 800 °C, and decreases with increasing temperature thereafter. Therefore, a pyrolysis temperature (Tpyrolysis) of 800 °C was chosen in this work to maximize the yield of gaseous PE pyrolyzates while minimizing the generation of tars and oils. Polycyclic aromatic hydrocarbons (PAHs), thought to be soot precursors [58], as well as heavier tars and oils may deactivate the catalysts and contaminate the samples [55]. As illustrated in Fig. 11, major detected pyrolyzates include methane, ethane, ethylene, propane, propylene, acetylene, butene, butadiene, ethylacetylene, benzene and hydrogen. A mass balance was performed in this case and over 95% of the polymer mass was accounted for in the mass of the detected gaseous pyrolyzates, which is in good agreement with the results of Conesa et al. [56]. A cursory examination of the CNT production from pyrolysis/combustion of either HDPE (milk jug) or LDPE (news paper wrap) did not reveal major differences in terms of morphology; however, a complete study has yet to be made and more characterization work is needed. Moreover, an additional cursory investigation on the effects of pre- or post-consumer (cleaned) polyethylene did not reveal major differences.

2.4.2 The Effect of the Oxidizer Gas on the Effluent Gas Compositions and CNT Structures

This process presented herein has been capable of generating CNTs under both pyrolytic and oxidative conditions, i.e., without and with oxygen addition in the venturi. Whereas under
pyrolytic conditions the hydrocarbon pyrolyzates of PE are the feedstock for CNT synthesis [59,60]; under oxidative conditions, also CO and even CO$_2$ are expected to contribute to CNT growth [12,22,61,62].

Figure 11: Chemical species detected under four different furnace operating purely pyrolytic or oxidative conditions. Postconsumer HDPE was used as feedstock (T$_{pyrolysis}$ = 800 °C, T$_{synthesis}$ = 750 °C, O$_2$ mole fraction at the venturi was 21%, the substrate/catalyst was 304 stainless steel).

Under pyrolytic conditions, comparisons of the detected chemical products at either the presence or absence of the catalyst reveal that LHC species were abundant, and that differences in those species were detectable before and after the synthesis, see Fig. 11 (‘pyrolysis’ versus ‘CNT synthesis under pyrolysis’). For instance, when CNTs were synthesized (Fig. 12a) from the pyrolysis products of 1 g batches PE, the cumulative mole fraction of LHCs decreased from 13.8% to 12.6%. These values correspond to carbon masses of 837 and 751 mg in the input and output of the catalyst section of the synthesis reactor; the difference of carbon mass being 86 mg. By comparison, the gravimetrically-measured generated CNT mass was 85mg; this verifies the mass
conservation of carbon and indicates little, if any, carbon losses during the synthesis process. This also shows the importance of LHCs as carbon sources for CNT growth. Moreover, by comparing the CNT yield (85 mg) to the input carbon mass (837 mg) in 1 g of polymer, a carbon conversion efficiency (carbon in CNTs/ carbon in the polymer) of 10% was calculated. The H₂ mole fraction increased from 1.2% to 1.7% which shows that the byproducts of the synthesis process are, indeed, enriched with hydrogen, see also similar results elsewhere in catalytic decomposition of hydrocarbons [63,64]. Therefore, this process turns out to be multi-functional, as it not only provides a value-added product (CNTs) but, also value-added byproducts similar to syngas, such as hydrogen and hydrocarbons [64,65].

Under oxidative conditions, the effluent gases of the pyrolysis furnace were mixed with oxygen-containing gases introduced to the venturi, to attain O₂ mole fractions of 17%, 21%, 25% and 50% therein. Upon auto-ignition, the pyrolyzates burned in nominally premixed flames, anchored at the throat of the venturi. The calculated average bulk equivalence ratios for all cases were fuel-rich (φ>2.0) and flames exhibited a bright yellow luminosity. Oxygen addition to the venturi and combustion at fuel-rich conditions consumed hydrocarbon pyrolyzates and, in turn, it is likely that combustion pyro-synthesized other hydrocarbons. As an example, the case of 21% oxygen addition is depicted in Fig. 11. Therein, it can be seen that the emissions of most of the monitored LHCs were drastically less than those emitted under pure pyrolysis. An exception was acetylene, whose mole fractions were much higher under oxidative conditions than under pyrolytic conditions. Hydrogen and water, formed in situ during combustion of the PE pyrolyzates, may have played the beneficial role of preventing catalyst deactivation and
poisoning by continuously cleaning its surface [49]. It was also found that the addition of a catalyst and the corresponding synthesis of CNT caused a small increase in H₂, a substantial reduction in CO₂, and a small reduction in CO, see Fig. 11. The H₂ content of the effluent gases was much higher under pyrolysis/combustion conditions (i.e., when a flame was present at the venturi) than under pyrolysis/pyrolysis conditions (i.e., the flame was absent). The most likely explanation for this difference is that the high combustion temperatures attained in the flame induced de-hydrogenation of hydrocarbon pyrolyzates, generation of radicals and, under the overall very fuel-rich conditions of these experiments (φ > 2.0), additional H₂ was eventually generated. While it is certainly true that part of the hydrogen is consumed by water formation, at fuel-rich condition no sufficient oxygen is available and a significant fraction of H₂ is therefore present in the combustion process. The hydrogen concentrations are consistent with thermodynamic equilibrium calculations. The limited increase of hydrogen mole fraction upon CNT synthesis in the pyrolysis/combustion case may be explained based on the fact that the generation of CNTs (which are basically hydrogen-free) from hydrocarbon feedstock releases hydrogen into the furnace effluent. On the other hand, possible generation of CNTs from CO feedstock (see for instance, CO + H₂ → C + H₂O [66,67]) can consume H₂, but apparently the former mechanism may be more prevalent. The difference of each individual hydrocarbon species before and after the CNT synthesis process was also measured. Whereas most LHC concentrations were slightly reduced during CNT synthesis, the reduction in acetylene (C₂H₂) was the most pronounced (Fig. 11). A carbon balance showed that the mass of CNT yield accounted for the observed reduction of carbon mass as the combustion gases passed through the
catalyst section of the synthesis reactor. This indicates that all carbon-bearing gases (LHCs, CO and CO₂) may have contributed as feedstock to CNT at this temperature.

Due to the exceedingly fuel-rich conditions maintained in these flames, CO was seen to increase with increasing O₂. At three of the tested O₂ mole fractions of 17%, 21% and 25% at the venturi, the corresponding flame-generated average CO mole fractions entering the synthesis chamber were: 7.60%, 9.06%, and 12.76%, respectively. Moreover, the corresponding average CO₂ mole fractions were: 3.88%, 5.3%, and 5.73%, respectively. In the case of 21% O₂ in the venturi, the hydrogen and unburned hydrocarbon mole fractions in the synthesis furnace were also measured, with the catalyst absent or present, and results were included in Fig. 11.

Figure 12: Electron microscopy images of pyrolysis based CNT ((a) SEM, (e) TEM, and (g) HRTEM), and combustion based CNT (SEM, (b) [O₂] = 17%, (c) [O₂] = 21%, (d) [O₂] = 25%; TEM, (f) [O₂] = 25%; HRTEM, (h) [O₂] = 25%). Post-consumer HDPE was used as feedstock ($T_{pyrolysis} = 800$ °C, $T_{synthesis} = 750$ °C, the substrate/catalyst was 304 stainless steel).
Regarding the characteristics of the combustion-generated CNT product shown in Fig. 12 b–d, the following observations can be made. As the oxygen mole fraction in the flame was increased from 17% to 25%, the CNT structures appear to be smoother and longer. A statistical analysis of the product diameter at the aforementioned three O\(_2\) mole fractions revealed corresponding mean diameters of 82, 52 and 38 nm, respectively. As corresponding CO mole fractions entering the synthesis chamber were 7.60%, 9.06%, and 12.76%, respectively, this observation may indicate that higher CO concentrations correlate with smaller CNT diameters. Similar observations have been made elsewhere by Hall et al.3 and by Zhang and Young [68]. SEM observations suggest that the surfaces of the pyrolysis-generated CNTs were not as smooth as those of combustion-generated CNTs, indicative of a larger concentration of wall defects or deposition of other carbonaceous materials on their surface. Corresponding TEM observations, nevertheless, revealed the existence of hollow tubular structures in the cases of both pyrolysis-generated CNTs (Fig. 12e) and combustion-generated CNTs (Fig. 12f). The explicit effects of oxygen on the resulting CNT quality are not clear at this point, even with the HRTEM examination of individual tubes (Fig. 12g for pyrolysis-generated CNT, and Fig. 12h for combustion-generated CNT).

2.4.3 The Effect of Catalysts on the CNT Product
A series of experiments was conducted to investigate the correlation of the catalyst layer identity with the characteristics of the resulting CNTs. Materials grown on uncoated 304 stainless-steel screens or on 304 stainless-steel screens, coated with either 4 nm thick cobalt (Co) or 4 nm thick nickel (Ni) layers, were examined by means of both SEM and TEM, see Fig. 13a–f, respectively.
Whereas nano-structural material could be identified in all cases, a variety of distinct features were observed on the cobalt-coated screens. Structures consisting of straight, tortuous or coiled (arrowed) shapes were observed. As shown in Fig. 13a, these structures are micrometers-long, but of various diameters. In contrast, CNTs generated on either the 4-nm Ni coated 304 SS or on the uncoated 304 SS had a rather uniform diameter distribution (Fig. 13b and c). Coiled or irregular structures were not present in these samples. TEM images of samples generated after deposition of 4-nm thick Co and Ni layers are shown in Fig. 13d and e. For the case of 4 nm Co, transparent regions including the side surface and the cross-section of the tube could be identified. The variance of tube diameters was significant ranging from approximately 20 to 100 nm. No striking difference in wall thickness was observed. Overall, nanostructures grown in the presence of a 4-nm-thick Ni catalyst appear to be more even than those in the presence of a 4 nm Co catalyst layer. However, due to the possible impact of sample preparation, definitive conclusions cannot be made at this point.

In the case of the 4-nm Ni coated meshes, the presence of catalyst particles (see arrow in Fig. 13e) was evident. However, using EDS, it was revealed that these metallic nanoparticles, attached at one end of the CNT, consisted not only of nickel but also iron, chromium, and manganese, which are typical components of the stainless-steel substrates. The exact contribution of the Ni catalyst on the CNT synthesis therefore remains uncertain at this point. In other words, this observation is in agreement with the fact that uncoated 304 stainless steel, consisting of several elements, also serves as a catalyst to CNT growth [69–71]. Finally, repeating the CNT synthesis with the same operating conditions but using stainless-steel meshes without addition of well-defined cobalt or
nickel coatings, resulted in the structures shown in Fig. 13c and f, and also in Figs. 7a and b & 12a and e. Experiments to measure yield were only performed using uncoated stainless-steel meshes. Wire meshes with extra catalysts coating (Co and Ni) have been costly in this study, since the coating process was outsourced. Thus, as the experiments to measure yield used large amounts of screens to collect measurable amounts of CNT, coated screens were not included.

Figure 13: Electron microscopy images of material grown from combustion effluents of PE pyrolyzates. Top row: SEMs of CNTs synthesized with a) 4-nm Co coated mesh; (b) 4-nm Ni coated mesh; (c) uncoated 304 SS mesh. Bottom row: TEMs of CNTs synthesized with (d) 4-nm Co coated mesh; (e) 4-nm Ni coated mesh; (f) uncoated 304 SS mesh.
2.5 Conclusions

The potential for a low-cost alternative feedstock for the growth of CNT, i.e., post-consumer polymers (waste plastics), has been demonstrated. Stand-alone pyrolysis of polymers, or pyrolysis followed by premixed combustion of the resulting gaseous pyrolyzates generate agents for CNT growth on catalytic surfaces. In these processes, sufficient concentrations of carbon-containing species (either LHCs alone, or a mixture of LHCs, CO and CO₂) as well as diatomic hydrogen and water (in the latter case) are formed in situ safely and economically from the thermal treatment of the polymers. Utilizing a high-temperature ceramic filter, process-generated particulates (soot) were removed prior to the synthesis stage. In the case of the pyrolysis/combustion process, this feature allows taking advantage of high fuel-to-oxygen ratios, as it precludes soot-contamination of the catalyst. CNTs were generated in time frames of 1 min, with typical lengths in the range of 1–5 µm, and mean diameters in the range of 30–85 nm; they are regular graphene-based, multi-walled CNTs. A scaled-up industrial system should be able to capture and utilize the energy released during the exothermic combustion of the waste plastics. This will offset the energy required to pyrolyze the solid plastics and to preheat the input gas, as these two processes require only a small fraction of the energy released during combustion [39,56,72]. This energy feedback would greatly improve the overall energy-efficiency of the process and, thus, it would further minimize the cost of the ensuing CNT product. Energy surplus may also be available.
2.6 Acknowledgements

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2.7 References


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CHAPTER THREE

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3. Catalytic Conversion of Wastes from the Bioethanol Production into Carbon Nanomaterials

Abstract

This work addressed the production of carbon nanomaterials (CNMs) by catalytic conversion of wastes from the bioethanol industry, in the form of either sugarcane bagasse or corn-derived distillers dried grains with solubles (DDGS). Both bagasse and DDGS were pyrolysed at temperatures in the range of 600-1000 °C. The pyrolyzate gases were then used as CNM growth agents by chemical vapor deposition on stainless steel meshes, serving as both catalysts and substrates. CNM synthesis temperatures of 750-1000 °C were explored, and it was determined that their growth was most pronounced at 1000 °C. The nanomaterials produced from pyrolysis of bagasse were in the form of long, straight, multi-wall nanotubes with smooth walls and axially-uniform diameters. Typical lengths were circa 50 μm and diameters were in the range of 20-80 nm. The nanomaterials produced from pyrolysis of DDGS were in the form of long, entangled, rope-like structures with rugged walls, and axially non-uniform diameters. Typical diameters were in the range of 100-300 nm and their lengths were in the tens of microns. This process also produces a bio-syngas byproduct that is enriched in hydrogen.

Keywords: Nanomaterials, Catalysis, Pyrolysis, Bioethanol, Sugarcane Bagasse, DDGS.
3.1 Introduction

The interest in biomass-derived energy has increased considerably, on a worldwide-basis, due to the necessity of finding renewable, clean-burning and CO$_2$-neutral energy resources to replace fossil fuels. Particularly, biomass-derived ethanol (bioethanol) has been viewed as a transportation fuel with the potential of replacing large amounts of petroleum-derived fuels [1, 2]. The requirement of reducing greenhouse gases (GHGs) in the atmosphere has also been widely discussed to mitigate global warming. The combustion of fossil fuels is responsible for 73% of the CO$_2$ generation, thereby partial replacement of fossil fuels by bio-ethanol would enable a reduction in the levels of CO$_2$ emissions. For instance, replacing gasoline with E-85, a typical biomass fuel blend that contains 85% bioethanol and 15% gasoline by volume, in a midsize passenger vehicle can reduce the GHG emissions by 41-61% per kilometer driven [2-5].

According to the Renewable Fuels Association (RFA), the world bioethanol production in 2008 was approximately 65.6 billion liters (17.3 billion gallons), representing a 24% increase in the production than the previous year [6]. This amount of ethanol replaced roughly 5% of the gasoline usage in 2008 [7]. The major producers of ethanol are the USA and Brazil, which together account for about 90% of worldwide production. The main feedstock for ethanol in USA is corn grains, whereas in Brazil is sugarcane [2, 3, 6].

Fermentation is the main process in the ethanol production from sugarcane; during this process a juice is generated which is used to obtain the ethanol. The solid residue from the fermentation process is a dried pulp known as sugarcane bagasse; approximately 0.225 kg of this waste is
generated for each 1 kg of sugarcane introduced to the process [8]. According to the National Supply Company of Brazilian Government (CONAB), the forecast of Brazilian ethanol production for the year 2009/10 is 28 billion liters, which will demand about 350 million tons of sugarcane and will generate approximately 80 million tons of bagasse. The numbers of generated bagasse are even greater when the sugarcane used to produce sugar is also considered: together, the Brazilian industries of sugar and ethanol processed about 630 million tons of sugarcane in 2009, which generated approximately 142 million tons of bagasse [9]. Sugarcane bagasse may be burned to produce energy and steam that are used within the ethanol plant or may be exported for a district heating system, thereby reducing the demand for fossil fuels [2, 8]. The sugarcane bagasse has a typical energy content of 17 MJ/kg, thus considering the total production of this waste in 2009 (142 Mt) up to 2400 GJ could be released as thermal energy [10].

Corn-grain-based ethanol production in North America has been rapidly increasing, from about 19 billion liters in 2006 to 38 billion liters in 2009 [11]. Ethanol industries convert corn into ethanol primarily by two processes: wet milling or dry grinding. In wet milling, the corn kernel is fractionated into primary components (starch, germ and fiber), which results in several process streams and co-products. The dry grind processing consists of six major stages: grinding, cooking, liquefaction, saccharification, fermentation, and separation. End products of dry grinding include ethanol fuel, carbon dioxide and distillers dried grains with solubles (DDGS). The dry grind plants are responsible for more than 70% of corn-based ethanol production due to lower capital costs and their higher yields of ethanol [3, 12, 13]. After the starch fraction of corn is fermented with selected yeasts and enzymes to produce ethanol and carbon dioxide, the
ethanol is removed by distillation and the remaining residues are dried producing the DDGS [13, 14]. Currently, DDGS is used as livestock feed due to its high protein content; however it also has high fiber content, which limits its use to ruminant diets as it could cause health problems in animals [12-15]. The generation of DDGS has increased along with the ethanol production, the amount of DDGS produced in the USA was about 31.5 million tons in 2009 [16]. Therefore, it is desirable to find new uses for DDGS to add value for this product and consequently to help reduce the cost of producing ethanol. The recovery of DDGS as a fuel could be used for power generation, since this material has an energy content of 27 MJ/kg which exceeds the energy content of lignite coals (10-20 MJ/kg) and approaches that of bituminous coals (30 MJ/kg) [17].

Waste-to-energy technology has been used to reduce the amount of residues entering in landfills and generate power without using non-renewable resources [18, 19]. Biomass waste (like sugarcane bagasse and DDGS) can be converted into useful forms of energy using various types of technologies: thermo-chemical, bio-chemical/biological or mechanical extraction. The thermo-chemical is the most popular technology, it includes the pyrolysis, combustion, gasification and liquefaction processes [8]. In the current study the pyrolysis process was used, wherein the waste biomass was decomposed by thermal treatment in an oxygen-free environment (N₂). The decomposition of biomass by thermal treatment to produce energy has been widely discussed, and has been proven to be cost-efficient and to produce low pollution indexes [2, 8, 10, 12, 17]. A process is presented herein, whereby solid biomass residues are pyrolyzed to generate potentially-useful gaseous effluents (containing CO, H₂ and hydrocarbons) while, at the same time, produce carbon nanomaterials (CNMs), such as CNTs, on catalytic substrates.
CNTs were discovered by Iijima in 1991, and consist of coaxial tubular graphene sheets, with lengths in the order of micrometers and diameters in the order of nanometers ($1 \times 10^{-9}$ m) [20]. The CNTs are materials with extraordinary mechanical, thermal and electrical properties, and they have a wide range of potential applications in energy management, electronics, structural materials and chemical processing [21-23]. A major attribute of a raw-material to produce CNTs is its capacity to provide a considerable source of gas-phase carbon [23]. This attribute can be satisfied by both the sugarcane bagasse and the corn-based DDGS, which are lignocellulosic biomasses (consists basically of cellulose, hemicelluloses, and lignin). Upon pyrolysis, they generate a large number of gaseous hydrocarbons, CO and CO$_2$ as well as H$_2$ and H$_2$O [5, 13]. In past years, a variety of synthesis techniques for CNTs have been developed: arc discharge, laser ablation, flame synthesis, and CVD [24]. However, the high cost to produce such materials limits their usage. To reduce the cost of CNTs, it is instrumental to reduce the expenses associated with the procurement of raw-materials and to reduce the production expenses. By using biomass wastes as feedstocks for CNT growth, the cost of raw-material can be minimized. Furthermore the process operating costs can be minimized by burning additional biomass to provide thermal energy for the pyrolysis and the CNT synthesis processes. Finally, a CO, H$_2$ and hydrocarbon containing gas is generated by the pyrolysis process which may have further value, akin to synthesis-gas generated from coal.

Aside of the carbon sources for CNT generation, another important factor in this process is the catalyst. As the formation of such nanostructures cannot be activated at the absence of a catalyst, identification of an effective and affordable catalyst is paramount. Currently popular catalyst
systems are typically found in the forms of either floating-oriented [25] or fixed substrate-based [26] configurations. Effective catalysts include, but are not limited to, iron (Fe) [27, 28], nickel (Ni) [29, 30] and cobalt (Co) [31]. Alloys that incorporate such elements in their compositions, e.g. stainless steel, have also been examined [32]. Particularly, stainless steel meshes have served as substrates, coated with a thin film of extra catalyst such as Ni [33]; even neat stainless steel has been reported to be a catalyst itself [32, 34]. This finding is important since use of stainless steel, a readily-available and economical commodity, can lower the cost of the production of CNMs. Consequently, this study utilized fine stainless steel meshes as both catalysts and substrates for growing CNMs. However, as the process of CNM formation depends on the interactions among carbon sources, catalysts, and process parameters, such as temperature, any changes in one of these factors can have a significant impact on the final products. Thus, an investigation on factors affecting the catalyst activity was also included in this study.

To allow for optimum pyrolysis and CNM synthesis conditions, the process presented herein separated the solid feedstock pyrolysis from the CNM synthesis and permitted both subprocesses to be operated independently. This allowed generation of suitable end-products.

An important technical feature incorporated in this process was the use of a high-collection-efficiency high-temperature ceramic (SiC) barrier filter, shown in Fig. 14, to prevent condensed matter pyrolyzates (soot, ashes, etc.) from depositing on the catalytic substrate and causing contamination. This was found to be an enabling step in this technology. This filter can be periodically regenerated thermally by exposing it to oxidizing gases at high temperature to destroy soot and, if needed, aerodynamically (by back-pulsing) to remove ashes.
3.2 Materials and Methods

3.2.1 Materials
The raw biomass feedstocks used in this study were: (i) sugarcane bagasse provided by a Brazilian ethanol producing company, this material was received in fiber form and was pulverized to particle sizes smaller than 500 µm using a household blender; (ii) corn-derived Distillers Dried Grains with Solubles (DDGS) provided by a North American ethanol-producing company, this material was used as received (grains about 500 µm, in diameter). Table 6 lists the chemical properties of these materials; carbon accounts for approximately half of their mass, whereas oxygen accounts for nearly one fifth of their mass.

3.2.2 Sample preparation
A ceramic boat was used to insert the raw materials (bagasse and DDGS) in the furnace; amounts of 4.0 grams were used in each experiment.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>O</th>
<th>K</th>
<th>H</th>
<th>S</th>
<th>N</th>
<th>P</th>
<th>Ca</th>
<th>Fe</th>
<th>Si</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bagasse</td>
<td>50.5</td>
<td>17.5</td>
<td>4.1</td>
<td>6.7</td>
<td>1.7</td>
<td>0.3</td>
<td>0.5</td>
<td>2.7</td>
<td>4.8</td>
<td>7.0</td>
<td>4.2</td>
</tr>
<tr>
<td>DDGS</td>
<td>48.2</td>
<td>17.8</td>
<td>7.5</td>
<td>7.5</td>
<td>6.7</td>
<td>3.7</td>
<td>3.2</td>
<td>0.6</td>
<td>0.5</td>
<td>0.3</td>
<td>3.9</td>
</tr>
</tbody>
</table>

The laboratory apparatus consists of a two laminar-flow, electrically-heated, muffle furnaces placed in series. Both furnaces were fitted with quartz tubes. The first furnace served as the pyrolyzer (37 mm ID x 870 mm), and the second furnace served as the CNM synthesis reactor (37 mm ID x 380 mm long). A silicon carbide (SiC) honeycomb barrier filter was placed inside
the quartz tube, between first and second furnace. This filter has a retention efficiency of 97% for soot particles bigger than 1 µm [35]. A schematic of the furnace is shown in Fig. 14.

Figure 14: Schematic of the furnace used in the experiments.

The raw biomass feedstocks were inserted into the first section of the furnace under a flow of inert gas. Nitrogen, at the flow rate of 3 l/min, ensured the absence of oxygen and, therefore, the raw materials decomposed under pyrolytic conditions. Thermal decomposition occurred under three different temperature settings in the first furnace (pyrolyzer), which had been preheated to 600, 800 and 1000 ºC.

The pyrolyzate gases were channeled to the second furnace (the CNM synthesis reactor), which was preheated to three different temperatures: 750 ºC, 900 ºC and 1000 ºC. Condensed-phase pyrolyzate components in the gas (soot and ashes) were filtered by a high-collection-efficiency (97%), high-temperature (>2500ºC) ceramic (silicon carbide) barrier filter, shown in Fig. 14, manufactured by Ibiden Inc.

Synthesis of carbon nanomaterials occurred by chemical vapor deposition (CVD) of the pyrolyzates on type 304 stainless steel screens. Such screens, mainly consisting of 67% iron, 18-20% chromium and 11% nickel, served as both the catalysts and the growth substrates. The
stainless steel screen was used as-received, without any pretreatment other than simple cleaning with acetone; pieces of 300×100 mm were rolled in cylindrical shapes with outside diameters of approx. about 40 mm, and were inserted in the quartz tube section of the second furnace. Upon insertion of a batch of biomass feedstock in the preheated pyrolysis furnace the evolution of CO and CO₂ gases was monitored in real-time with on-line instruments. Upon cessation of the evolution of these gases, the catalytic substrates were kept in the synthesis chamber at temperature for an extra five minutes to ensure the completion of the feedstock pyrolysis process. Thereafter, a cooling process was initiated by turning the furnaces off. The apparatus was cooled down to at least 200 °C under nitrogen, before the mesh was removed for further analysis. The duration of each experiment was in the order of minutes; as determined by the time elapsed between the onset and the termination of the evolution of CO and CO₂ in the pyrolysis effluents of these two oxygen-containing raw materials.

3.2.3 Catalyst Investigation

Type 304 stainless steel wire cloths were purchased from McMaster Co., and were in the form of 400×400 meshes, with 25 µm wire diameter, and chemical components according to ASTM E2016 specification: Cr (18-20,0%), Ni (8-10,5%), Mn (≤2,0%), Si (≤1,0%), N (≤0,1%), C (≤0,08%), P (≤0,05%), S (≤0,03%), and Fe (balance) [36]. Samples were cut to 25×25 mm squares, were immersed in a solution of 10% nitric acid, and were rinsed with the de-ionized water. In order to examine sample uniformity, 10% of the cleaned samples were randomly chosen to be examined by SEM. Average grain sizes were recorded and compared. Chemical compositions were also determined by energy dispersive X-ray spectroscopy (EDX). The
stainless steel meshes were inserted in the middle of the synthesis chamber, see Fig. 14, and were subjected to one of the following two sets of operating conditions: (a) Control experiments, where 3 l/min of nitrogen were channeled through the synthesis chamber. (b) Actual experiments, where 3 l/min carbon-containing gases (i.e., sugarcane bagasse and DDGS pyrolyzates) were channeled through the synthesis chamber. Three different synthesis temperatures were applied: 750, 900 and 1000 °C. The durations of these tests were identical. The treated samples were again examined using SEM.

3.2.4 Effluent analysis and sample characterization

During the experiments, an on-line dual infrared analyzer (California Analytical Instrument, Model 200) was used to monitor the CO and CO₂ emissions. Light hydrocarbon gases (LHCs), generated during the experiments, were monitored off-line at the exit of the synthesis furnace. Gases were withdrawn at a rate of 0.5 ml/min, using syringes mounted on a dual syringe pump. Two samples were extracted simultaneously. Analysis was performed by gas chromatography (GC), with a HP 6890-series instrument equipped with two parallel columns, one coupled to a flame ionization detector, the other to a thermal conductivity detectors (GC-FID and TCD). Control experiments at the absence of the catalyst substrate screens were also performed and the composition of the pyrolyzate gases was likewise analyzed.

Morphological examination of the carbon nanostructure product was performed using Scanning Electronic Microscopy (SEM) and Transmission Electron Microscopy (TEM). Random pieces of the mesh were removed and placed directly on the SEM imaging stage. SEM analysis was conducted with a Hitachi 4800 instrument, at an accelerating voltage of 3 kV, and a working
distance of 8.2 mm. For TEM analysis, the meshes were sonicated in a neat ethanol solution and a drop of the solution was deposited on a TEM holey carbon grid. Both an environmental TEM (model JEOL 1010, with an accelerating voltage of 70 kV) and a high-resolution TEM (model JEOL 2010, with an accelerating voltage of 200 kV) were used. Experiments were repeated several times in order to gather amounts of carbon nanomaterials that are sufficient for subsequent characterization. To remove the carbon nanomaterials from the catalytic substrate screens, sonication in neat ethanol was again implemented. This was followed by gentle heating, evaporation of the alcohol and air-drying of the precipitating materials. Collected powders were then examined by Thermogravimetric Analysis (using a TGA model HR V5.4A, under a N₂ flow at a ramp rate of 10 °C/min) and Raman spectroscopy (using a Micro-Raman RENISHAW with an excitation laser wavelength of 632.8 nm).

3.3 Results and discussion

3.3.1 Analysis of pyrolyzate gases

In this study, the pyrolyzates gases of sugarcane bagasse and corn-based DDGS functioned as feedstock gases for generation of carbon nanomaterials (CNM). This section presents the composition of these gases at the exit of the synthesis furnace, both at the absence and in the presence of the catalytic substrates (stainless steel meshes) where CNM were grown. Thereby, the effects of the catalytic CNM synthesis process on the composition of the aforesaid pyrolyzate gases are examined. Assessment of the composition of the pyrolyzates at the exit of the synthesis furnace is, also, important in the event that the effluent will be further utilized downstream as a bio-syngas [37]. Table 7 shows the total yields of detected light hydrocarbons (LHCs) for each
experiment, with or without the meshes. Calculated yields of the most prominent hydrocarbon species: methane (CH\textsubscript{4}), ethylene (C\textsubscript{2}H\textsubscript{4}), acetylene (C\textsubscript{2}H\textsubscript{2}) and benzene (C\textsubscript{6}H\textsubscript{6}) are shown in Fig. 15. Traces of other compounds were also detected: toluene, ethane, propylene, propyne, ethylacetylene and ethylbenzene. The mole fractions of all detected LHCs increased with increasing pyrolysis temperature in the range of 600-1000 °C (at a constant synthesis temperature of 1000 °C). Furthermore, at each temperature setting, the mole fractions of all detected LHCs were observed to decrease when the catalyst substrate (meshes) were present.

Table 7: Catalysis and pyrolysis behavior of each tested condition

<table>
<thead>
<tr>
<th></th>
<th>Temp. (°C)</th>
<th>Reaction time (s)</th>
<th>Mesh wt. rise (mg)</th>
<th>Ave. growth (mg/s)</th>
<th>Carbon recovery (%)\textsuperscript{3}</th>
<th>Total LHCs (mg)\textsuperscript{4}</th>
<th>H\textsubscript{2} emissions (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Without mesh</td>
<td>With mesh</td>
</tr>
<tr>
<td>BAGASSE</td>
<td>600</td>
<td>180</td>
<td>202</td>
<td>1.1</td>
<td>10.0</td>
<td>844</td>
<td>352</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>110</td>
<td>146</td>
<td>1.3</td>
<td>7.2</td>
<td>753</td>
<td>324</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>70</td>
<td>117</td>
<td>1.7</td>
<td>5.8</td>
<td>759</td>
<td>491</td>
</tr>
<tr>
<td>DDGS</td>
<td>600</td>
<td>250</td>
<td>190</td>
<td>0.8</td>
<td>9.9</td>
<td>859</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>150</td>
<td>143</td>
<td>1.0</td>
<td>7.4</td>
<td>615</td>
<td>436</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>100</td>
<td>137</td>
<td>1.4</td>
<td>7.1</td>
<td>613</td>
<td>503</td>
</tr>
</tbody>
</table>

\textsuperscript{3} Ratio between mesh weights rises and amounts of carbon inserted in the system.

\textsuperscript{4} Mass yield estimated based on the 4 g of biomass inserted in the furnace.
Calculated yields of CO, CO\textsubscript{2} and H\textsubscript{2} are also included in Fig. 15. The former two gases (CO and CO\textsubscript{2}) are typically found in pyrolysis products of biomass, as it contains large amounts of oxygen in its structure, see Table 7. CO emissions from bagasse pyrolysis were in the range of 5.0-13.0\% (340-480 mg/g), whereas those from DDGS were lower, ranging from 2.7-7.3\% (140-220 mg/g). CO\textsubscript{2} emissions from bagasse pyrolysis were in the range of 2.0-6.0\% (220-340 mg/g), whereas those from DDGS were lower, ranging from 1.6-4.1\% (130-190 mg/g). Detected H\textsubscript{2} emissions from either bagasse or DDGS pyrolysis were in the range of 0.6-4.3\% (2-11 mg/g). The mole fractions of these three pyrolyzate gases, CO, CO\textsubscript{2} and H\textsubscript{2}, increased with increasing pyrolysis temperature in the range of 600-1000 °C, since pyrolysis became progressively more intense as the temperature was elevated. Moreover, the mole fractions of H\textsubscript{2} in all cases were observed to increase when the catalyst substrate (meshes) were present, as shown in Table 7. The volume fraction of hydrogen was as high as 4.2\% at the exit of the reactor. However, it should be noted that the flow of inert gas was not optimized in this study, hence, the volumetric hydrogen content of the effluent gas can be greatly increased if a much lower flowrate of nitrogen is used in the pyrolysis process. The presence of the catalyst did not have consistent effects on the CO and CO\textsubscript{2} emissions; in some cases a mild increase was observed whereas in some other cases a mild decrease was recorded, typically within experimental error.
Figure 15: Mass yields (in mg/g) of major pyrolysis products of: A) sugarcane bagasse, and B) corn-based DDGS.

A noteworthy trend emerging from the results of Table 8 and Fig. 15 is that all detected light hydrocarbon species were partially depleted at the presence of catalytic meshes. This indicates that they are instrumental in the formation process of carbon nanomaterials. Several previous investigations showed that the hydrocarbons can be used as an important carbon feedstock in the production of CNTs with the CVD method [38-45]. The prominent detected LHC species herein is methane (accounting for 30-50% of the total LHCs), followed by ethylene and benzene in most cases. Methane is the most thermally-stable hydrocarbon that undergoes the least pyrolytic decomposition at high temperatures. In fact, Kong et al. [38] investigated the use of methane as a
carbon source for CNTs by chemical vapor deposition at 1000 °C; they succeeded in producing high-quality single-walled CNTs.

In this work, the catalyst system induced thermal dehydrogenation reactions. Baker et al. [46, 47] studied the growth of carbon fibers and reported that the catalytic decomposition of hydrocarbon sources start on the active transition metal surfaces. A transition metal catalyst was then used to further “crack” the hydrocarbon gases into carbon and hydrogen [23]. Equation 1 below illustrates this process, in which carbon and H₂ are formed from hydrocarbons [48].

\[
C_xH_y \rightarrow xC + \frac{1}{2}y \text{H}_2
\]  

(1)

Thereafter, diffusion of carbon into the metal particles takes place until the solution becomes saturated. The supersaturation of the solution results in precipitation of carbon on the metal surface, leading to the formation of CNMs. Ranges of the weight increment of the mesh, \( \Delta W_{\text{mesh}} \), and of the corresponding carbon recovery (i.e. \( \Delta W_{\text{mesh}} / W_{\text{carbon in biomass}} \)) are shown in Table 7. The latter parameter illustrates the partition of the chemical reaction products between the solid-phase species (CNM) and the gas-phase species. The experiments conducted at a pyrolysis temperature of 600 °C resulted in the highest \( \Delta W_{\text{mesh}} \) for both types of biomass; for sugarcane bagasse, \( \Delta W_{\text{mesh}} = 221 \text{ mg} \); whereas for DDGS, \( \Delta W_{\text{mesh}} = 209 \text{ mg} \). In both cases, 4 grams of biomass were pyrolyzed.

The real-time monitoring of the evolution of CO and CO₂ indicated that using bagasse as feedstock the pyrolysis lasted for 180s at 600 °C and 70s at 1000 °C. CNM synthesis times are expected to be equal or shorter than pyrolysis times. For experiments using DDGS as feedstock
the pyrolysis times were about 250s at 600 °C, and 100s at 1000 °C. During those periods CNMs grew to 117-202 mg in the bagasse experiments, and 137-190 mg in the DDGS, where the lower values represent the pyrolysis temperature of 1000 °C. Assuming that CNM synthesis times are equal or shorter than pyrolysis times, average minimum CNM growth rates were calculated to be in the range of 1.1-1.7 mg/s when bagasse was used as feedstock and 0.8-1.4 mg/s when DDGS was used as feedstock. Reaction times and average growths of produced materials are showed on Table 7. Instantaneous growth rates were not observed.

Regarding the major hydrocarbon gases, the pyrolyzates of DDGS contained 2-3 times more acetylene than those from sugarcane bagasse, see Fig. 15. To the contrary, the pyrolyzates of bagasse contained much more ethylene, whereas the partial pressures of methane and benzene were overall comparable. It may be worth noticing that such hydrocarbon gases have been extensively used before elsewhere as CNM feedstocks [40-45].

Experiments were repeated in triplicate. Differences of detected species among the three runs were reasonably small; for instance, the measurement uncertainty for hydrogen amounted to 0.3-4.4% in these runs.

3.3.2 Analysis of generated CNM

The particulate matters found on the stainless steel meshes, at pyrolysis temperatures ranging from 600 to 1000 °C, in combination with synthesis temperatures in the range of 750-1000 °C, were characterized by SEM, TEM, TGA and Raman spectroscopy.
3.3.2.1 Microstructural analysis

Figure 16: SEM images of carbon nanomaterials generated by passing sugarcane bagasse pyrolyzates through catalyst substrates – Left column (A, B): $T_{\text{pyrolysis}} = 600 \degree C$; Right column (C, D): $T_{\text{pyrolysis}} = 1000 \degree C$. $T_{\text{synthesis}} = 1000 \degree C$ in both cases.

Scanning Electron Microscopy (SEM) was used to inspect the catalyst substrates in order to determine whether nanomaterials were formed. Little growth of CNTs was evident at synthesis temperatures lower than 1000 °C. Figs 16 and 17, respectively, show the SEM images, with different magnification, of synthesized materials from sugarcane bagasse and DDGS. In each figure, images A and B correspond to the waste biomass pyrolysis at 600 °C, whereas images C
and D correspond to the pyrolysis at 1000 °C. SEM images show a high number density of entangled nanomaterials, non-uniformly covering the catalyst mesh in all conditions.

Figure 17: SEM images of carbon nanomaterials generated by passing corn-based DDGS pyrolyzates through catalyzed substates - Left column (A, B): $T_{\text{pyrolysis}} = 600 \, ^\circ\text{C}$; Right column (C, D): $T_{\text{pyrolysis}} = 1000 \, ^\circ\text{C}$. $T_{\text{synthesis}} = 1000 \, ^\circ\text{C}$ in both cases.

The SEM images of the nanomaterials synthesized from sugarcane bagasse, Fig. 16, show cylindrical nanomaterials covering the catalyst surfaces. The lengths of these nano-cylinders were in the order of 50 μm. Experiments at pyrolysis temperatures of 1000 °C produced a smaller population of nanomaterials, which is consistent to the smaller measured $\Delta W_{\text{mesh}}$ at this condition (see Table 7). Figs 16A and 16C illustrate that the nanomaterials are in the form of
long fibers; whereas Figs 16B and 16D, taken at higher magnifications, show that the fibers have diameters in the range of 20-80 nm. The nanomaterials corresponding to the highest pyrolysis temperature (1000ºC) appear to be less entangled and possess straighter shapes.

Experiments that used corn-based DDGS as raw material, generated the nanomaterials shown in the SEM images of Fig. 17, which show high populations of nano-materials, completely covering the catalyst meshes. As shown in Figs 17A and 17C the materials have twisted and crooked forms with irregular shapes and rugged surfaces. Figures 17B and 17D, taken at higher magnifications, show that the nanomaterials have diameters in the order of 100-200 nm.

Transmission Electron Microscopy (TEM) was used for detailed structural analysis of the nanomaterials. TEM images, with different magnification, of the materials produced from pyrolyzates of sugarcane bagasse are shown in Fig. 18; whereas those produced from DDGS pyrolysis are shown in Fig. 19. Again, in each figure, images A, B and C correspond to the waste biomass pyrolysis at 600 ºC, whereas images D, E and F correspond to the pyrolysis at 1000 ºC. Images obtained using the high-resolution TEM are shown in Figs C and F for both wastes. In the case of bagasse, see Fig. 18, TEM images show that the produced materials have a tubular form, which is characteristic of carbon nanotubes (CNTs). These long, straight, smooth internal- and external-surfaced CNTs have several possibilities of technological applications due to their exceptional properties [21-23]. Whereas, in the case of DDGS, see Fig. 19, TEM images show that carbon nanomaterials were produced, including both CNTs and rugged rope-like structures.
Carbon nanotubes are classified as single-walled carbon nanotubes (SWNTs) or multi-walled carbon nanotubes (MWNTs). The SWNTs consist of a single graphene sheet rolled to form a cylindrical tube, and MWNTs are formed by a set of concentric single wall nanotubes [24]. TEM images revealed that the carbon nanotubes produced in this study have multiple walls, i.e. they can be classified as MWNTs. Examinations of the wall structures (shown in Figures 18C, 18F, 19C and 19F) indicate the presence of parallel graphene layers around the hollow cavity, especially in the case of Figs. 19 E and F.

Examination of the CNMs produced by the two biomass feedstocks of this study revealed very different structures (tubes versus ropes). However, it is not possible to attribute such a difference to a single carbon growth agent present in the feedstock pyrolyzates. For instance, although the emissions of acetylene were higher from DDGS, the emissions of other species such as ethylene were higher from bagasse. Besides, the mineral composition of the two feedstocks is very different, as listed in Table 6, a fact that further complicates the interpretation. Particularly, low boiling point elements, such as phosphorous, P, and sulfur, S, (whose boiling points of 280 °C and 445 °C are lower than the pyrolysis furnace temperatures of 600-1000 °C) have been suggested elsewhere as influencing the structure of CNMs [49-51]. In this study, the amounts of these elements in the two feedstocks varied widely ($P_{\text{DDGS}}/P_{\text{bagasse}} = 6.4$ and $S_{\text{DDGS}}/S_{\text{bagasse}} \approx 4$), thus their possible effects on CNM structures cannot be excluded.

The catalytic effects of minerals present in the feedstock, such as K, N, P, and S, on CNM growth were not examined in this study. However, Tibbetts and co-workers [49], Xie and co-workers [50], and Benissad-Aissani and co-workers [51] have presented evidence that S and P in
particular affect the growth of CNMs. The presence of sulfur in catalyst particles was found to be effective in moving the alloy’s melting point away from the eutectic temperature, thus changing the rate of CNM nucleation [49]. Furthermore, Xie et al. [50] proposed that the non-homogeneous distributions of metal-sulfur compounds (e.g. FeS) on the catalyst surface may be the source of irregular CNM structures. Though phosphorous may also cause a similar effect on CNM structures [51], the joint effects of various mineral elements as either catalyst promoters or inhibitors are still unclear.
Figure 18: TEM images of carbon nanomaterials generated by passing sugarcane bagasse pyrolyzates through catalyzed substates - Left column (A, B, C): Tpyrolysis = 600 °C; Right column (D, E, F): Tpyrolysis = 1000 °C.
Figure 19: TEM images of carbon nanomaterials generated by passing corn-based DDGS pyrolyzates through catalyzed substates - Left column (A, B, C): $T_{\text{pyrolysis}} = 600 \, ^\circ\text{C}$; Right column (D, E, F): $T_{\text{pyrolysis}} = 1000 \, ^\circ\text{C}$. 
TEM and SEM images often show tiny dark points at the tips of produced CNM. These have been identified by EDX to be metallic particles that were incorporated into the nanotubes during their catalytic growth process. Based on EDX measurements, the major metallic elements are chromium (Cr), iron (Fe), and nickel (Ni), which are the major components of the stainless steel substrates. Their corresponding weight percentages are 17%, 64% and 11%, which are in agreement with the chemical composition of the stainless steel, as given on Table 6. Other elements detected in the metallic particles include Si, S, and P, however, the amounts of S, or P, could not be accurately assessed by EDX. Some other impurities may also be expected to be present, thus purification processes are often used to reduce the presence of undesired components [52].

3.3.2.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) in nitrogen was used to determine the thermal characteristics of the generated nanocarbons. This is important, as heat treatment is a method that is often used for CNM purification [52]. A limited number of experiments revealed that CNM produced from both sugarcane bagasse and DDGS experience an initial weight loss at temperatures up to 300 °C, possibly attributable to adsorbed moisture and semi-volatile hydrocarbons. Nanocarbons produced with the lower pyrolysis temperature (600 °C) experienced a higher initial weight loss (11-14%), whereas those produced with the higher pyrolysis temperature (1000 °C) experienced a lower initial weight loss (7-10%). Thereafter, the weight of both materials remained stable with increasing temperature until the final temperature of 800 °C was reached.
3.3.2.3 Raman Spectroscopy

Raman spectroscopy conveys information on the structure and properties of carbon nanomaterials and enables the differentiation between nanotubes, graphite and amorphous carbon. Carbon nanotubes typically have ordered structures that generate well-defined bands in the Raman spectrum.

![Raman Spectroscopy Results](image)

**Figure 20:** Raman spectroscopy results for carbon nanomaterials generated by passing (A) sugarcane bagasse or (B) corn-based DDGS pyrolyzates through catalyzed substrates. Pyrolysis temperatures were 600 and 1000 °C.

Figs. 20 A and B show Raman spectra of nanomaterials generated by passing sugarcane bagasse, and corn-based DDGS pyrolyzates, respectively, through substrate catalysts (meshes). Feedstock pyrolysis temperatures were 600 and 1000 °C. Results showed that the spectra of the produced nano materials included two peaks at 1350 cm\(^{-1}\) (D band) and 1575 cm\(^{-1}\) (G band). The latter (G band) reflects the graphitic ordering of the material structures. The former (D band) reflects structural imperfections in the graphite sheets, such as impurities/defects in the materials. [53, 54]. Generally, the structure of CNTs may be evaluated by the \(I_G/I_D\) ratio between the intensities of G and D bands. A larger \(I_G/I_D\) ratio indicates a higher degree of structural ordering.
and purity for the nanomaterials [28]. The $I_G/I_D$ ratio of the samples was higher in the case of nanomaterials produced from bagasse than in the case of those produced from DDGS. It also increased with the synthesis temperature. For nanomaterials produced from the bagasse feedstock, $I_G/I_D=1.25$ at 1000 °C and $I_G/I_D=1.14$ at 600 °C. For nanomaterials produced from the DDGS feedstock, $I_G/I_D=0.89$ at 1000 °C and $I_G/I_D=1.83$ at 600 °C. The results indicate that nanomaterials generated from bagasse were of relatively higher purity and/or had lower defects inside the graphite sheet than those generated from DDGS. This finding supports the observations made from SEM and TEM images that nanocarbons generated from bagasse are multi-wall nanotubes, whereas most of those generated from DDGS do not have a tubular structure. Furthermore, higher synthesis temperatures were more favorable to the structures of the nanomaterials.

The origin of a third peak at 2633 cm$^{-1}$ (often referred to as the 2-D band) is from the two phonon double resonance Raman process [55]. This indicates the presence of parallel graphitic layers of samples synthesized from bagasse pyrolyzates, which is consistent with the HRTEM images. By contrast, those synthesized from DDGS pyrolyzates show weak, if, any, 2-D band peaks, which indicates the absence of parallel graphitic layers. The widths of all the displayed peaks (D, G and 2D) indicate the crystallinity of the samples, i.e, narrow peaks indicate better crystal ordering. In this study, the samples synthesized from bagasse pyrolyzates have narrower width than those from DDGS, indicating a better crystal ordering [56].
3.3.3 Effects of temperature and reaction environment on the catalyst morphology

Among the three synthesis reactor temperatures explored herein (750, 900, and 1000 °C), only the highest one produced good yields of CNMs. The formation of CNMs depends on the interaction between the carbon-bearing growth agents and the catalyst, the intensity of which depends on temperature. While in the case of these biomass-based feedstocks the optimum temperature (based on the yield) was 1000 °C, it may be worth mentioning that when waste plastics were used as a feedstock 750 °C was the optimum temperature [34]. The SEM photograph of Fig. 21A shows the surface morphology of untreated stainless steel, whereas Figs 21B, 21C and 21D show the surface morphology of stainless steel heat-treated under nitrogen. Upon heat-treatment, individual substrate catalyst particles (grains) grew and their edges became sharper at higher temperatures.
Figure 21: SEM images of catalyst surfaces before (A) and after heat treatments (B–F). Surfaces (B–D) were exposed to nitrogen, whereas surfaces (E–G) were exposed to the pyrolysis gases of sugarcane bagasse. The images are displayed according to the heat-treatment temperatures.

However, when pyrolysis gases of biomass were present (Figs 21E, 21F and 21G) a similar observation could not be made, either because the grains did not grow correspondingly or
because they were covered with carbon deposits masking their boundaries. At the highest synthesis reactor temperature, 1000 °C, growth of CNMs occurred. Close observation of the catalyst surface (Fig. 21G) showed the surface is covered with a deposit substrate, possibly metal carbides, on which CNMs grow, analogous to a two-step growth mechanism [24]. In fact, comparing the SEM images of bagasse-derived CNTs of Figs 16 with those of the catalyst surface of Figs 21D and 21G, no obvious correlation between the catalyst size and CNT diameters becomes apparent. This is because the CNT growth does not appear to be in direct contact with the catalyst surface, as illustrated in Fig. 21G.

A two-step CNM growth has been reported previously at the presence of “metal dusting” [24]. Metal dusting is a form of corrosion that occurs when metals are exposed to environments containing carbon-bearing gases. Rapid uptake of carbon into the metal leads to supersaturation and formation of metastable carbides [57]. Ensuing decomposition of the carbides results in loosely adherent metallic particles, which can then act as catalysts for further carbon deposition and CNT growth. Taking into account the fact that the pyrolysis products of either sugarcane bagasse or DDGS contain high concentrations of active carbon sources (carbon monoxide and a multitude of hydrocarbon species), it may be expected that such gaseous components provide a suitable environment for the formation of metal dusting, especially since a catalyst (alloy steel) is present in the reaction [57]. Therefore it is plausible, that such catalytic conversion of wastes from the bioethanol production involves metal dusting as a critical intermediate reaction process for CNM formation. This may also explain why reaction temperatures need to be as high as
1000 °C to facilitate such waste-to-CNM conversion, since at low temperatures the rate of the metal dusting generation is not significant.

3.4 Conclusions

Carbon nanomaterials were successfully generated by pyrolysis of waste residues from bioethanol production, both sugarcane bagasse and corn-based distillers dried grains with solubles (DDGS). These biomass residues were pyrolyzed in nitrogen at 600-1000 °C, and their pyrolyzate gases were used to grow carbon nanomaterials on stainless steel substrates, at an optimized synthesis temperature of 1000 °C. The gas phase pyrolyzates of the two biomasses included light-hydrocarbons, hydrogen, carbon monoxide and carbon dioxide. Synthesis of the nanomaterials consistently depleted the concentrations of the light hydrocarbons (most notably of methane, ethylene, acetylene and benzene), therefore, these gases were considered to be the major CNM growth agents.

The nanomaterials produced from pyrolysis of bagasse were in the form of long, straight, tubular structures with smooth walls and axially-uniform diameters. Typical lengths were in the order of 50 µm and diameters were in the range of 20-50 nm. They were classified as multi-wall carbon nanotubes. A more uniform CNT product was obtained with the higher pyrolysis temperature.

The nanomaterials produced from pyrolysis of DDGS were in the form of long, entangled, rope-like structures with rugged walls, and axially non-uniform diameters. Typical diameters were in the range of 100-300 nm, and their lengths were in the tens of microns.
The effluents of the synthesis chamber, in either case, were gases with considerable energy-content, as they included substantial amounts of carbon monoxide, light hydrocarbons and hydrogen. Therefore, it may be possible to utilize such a bio-syngas for power generation or other forms of co-generation. Alternatively, hydrogen may be separated for use in the transportation industry. The effect of synthesis temperature on such catalytic conversion was manifested through changes of catalyst particle size. At the high temperature of 1000 °C stainless steels was shown to be an effective low-cost catalyst for CNM generation through a two-step growth mechanism. Production of added-value byproducts, such as nanocarbons and bio-syngas, can supplement the production of ethanol from the biomass-related industries.

3.5 Acknowledgements

The authors would like to thank the CNPQ-Brazil for financing the period of the M.Sc. Joner O. Alves at Northeastern University (USA). Chuanwei Zhuo would like to thank Mr. William Fowle and Dr. Yong Zhang for SEM and TEM support. The support provided by CAPES (Grant: 04/CII-2008 - Rede Nanobiotec-Brasil) is also greatly appreciated. The authors also thank the Global Ethanol Company for providing samples for this study.

3.6 References


CHAPTER FOUR


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4. Synthesis of Carbon Nanomaterials through Up-Cycling

Agricultural and Municipal Solid Wastes

Abstract

This work addresses the synthesis of carbon nanomaterials (CNMs) by up-cycling common solid wastes. These feedstocks could supersede the use of costly and often toxic or highly flammable chemicals, such as hydrocarbon gases, carbon monoxide, and hydrogen, which are commonly used as feedstocks in current nanomanufacturing processes for CNMs. Agricultural sugar cane bagasse and corn residues, scrap tire chips, and postconsumer polyethylene (PE) and polyethylene terephthalate (PET) bottle shreddings were either thermally treated by sole pyrolysis or by sequential pyrolysis and partial oxidation. The resulting gaseous carbon-bearing effluents were then channeled into a heated reactor. CNMs, including carbon nanotubes, were catalytically synthesized therein on stainless steel meshes. This work revealed that the structure of the resulting CNMs is determined by the feedstock type, through the disparate mixtures of carbon-bearing gases generated when different feedstocks are pyrolyzed. CNM characterization was conducted by scanning and transmission electron microscopy as well as by Raman spectroscopy and by thermogravimetric analysis. Gas chromatography was used to characterize the gases in the synthesis chamber. This work demonstrated an alternative method for efficient manufacturing of CNMs using both biodegradable and nonbiodegradable agricultural and municipal carbonaceous wastes.
Keywords: Recycled Waste Plastics; Sugarcane bagasse; DDGS; Tires; Pyrolysis; Combustion; CVD; Catalyst; CNTs; CNMs

4.1 Introduction

In the year 2011, the global production of carbon nanomaterials (CNMs) was around 3500 tons, and it is projected to expand at a compound annual growth rate of 30.6%.\(^1\) Expanding markets for applications of CNMs, such as nanotubes (CNTs) and nanofibers (CNFs), place ever-increasing demands on lowering their production costs. Applications for CNTs and CNFs already exist,\(^2\)−\(^5\) and applications of carbon nanoropes (CNRs) may be identified.\(^6\) Current technologies for CNM generation require intensive consumption of premium feedstocks and, often, of costly catalysts; they also require an input of external energy.\(^7\) Industrial-scale production of CNMs is typically achieved through chemical vapor deposition (CVD) methods, \(^8,9\) which consume a variety of expensive premium chemical feedstocks, such as ethylene,\(^10,11\) carbon monoxide (CO),\(^12–14\) and hydrogen (H\(_2\)),\(^13\) or by flame synthesis techniques,\(^15\) which also consume premium feedstock fuels. Additionally, CVD methods are energy-intensive.\(^16–18\) Thus, there is a pressing need for resource-benign and energy-benign, cost-effective nanomanufacturing processes. In the search for sustainable alternatives, it would be prudent to explore renewable and replenishable feedstocks, such as those found in municipal, industrial, agricultural recycling streams. This work utilizes waste solid feedstocks in a novel sequential feedstock pyrolysis, partial oxidation, and CVD-synthesis method, developed in this laboratory, to generate CNMs.\(^19,20\) Both biodegradable and nonbiodegradable feedstocks have been
experimented with, including biomass residues from the production of bioethanol and sugar, postconsumer plastics used in food and beverage packaging, and scrap automobile tires. These wastes are generated in ever-increasing numbers and, hence, their supply streams are abundant.

To convert the granulated solid hydrocarbon feedstocks to CNMs, this method first pyrolyzes them in a furnace. Pyrolysis occurs in an inert nitrogen carrier gas. The gaseous pyrolyzates then flow into a venturi where they are thoroughly mixed either with preheated oxygen-containing gases (such as air) or with additional inert gases. In the former case, the oxygen, nitrogen, and pyrolyzate charge autoignites at the exit of the venturi, forming a premixed flame. The fuel to oxygen ratio is preadjusted to be fuel-rich, i.e., oxygen-deficient. This ensures that there are sufficient amounts of carbon-bearing compounds, hydrogen, and water vapor in the partial oxidation effluent, as needed for the growth of CNMs. The partial oxidation effluent then enters the second furnace where it encounters fixed catalyst substrates, such as stainless steel screens. Growth of CNMs occurs on the catalyst substrates. To prevent soot (which may be generated in the flame) from entering the second furnace and contaminating the catalyst substrates, a high-temperature ceramic barrier filter is inserted in the furnace, downstream of the flame. This feature allows operation of the apparatus above and beyond the equivalence ratio that corresponds to the soot onset limit. The ceramic filter may be periodically thermally regenerated in situ, at an elevated temperature in the air, to burn any entrained soot particles. In summary, this process incorporates the following unique features: (a) It pyrolyzes or gasifies solid wastes to generate gaseous carbon-bearing components. (b) The pyrolysis and the CNM synthesis occur in two separated stages, which afford individual control of the subprocess
conditions. (c) The risks of handling highly reactive gases (such as H₂), and/or highly toxic gases (such as CO), are eliminated as they are generated in situ in an inert gas. Finally, (d) this process can generate a hydrogen-enriched syngas.

Moreover, this process can be designed to be energy efficient. For instance, Jinno et al.23 measured the heat of pyrolysis of polyethylene (PE) to be 254 kJ/kg, independently of the heating rate. Comparing the heat of pyrolysis to the heating value (energy content) of this polymer, which is 46 000 kJ/kg,24 it becomes evident that a small fraction of the heat released during combustion may be fed back and pyrolyze this solid fuel. Similarly, the energy fluxes necessary to pyrolyze polypropylene (PP) and polystyrene (PS) are 423 and 1500 kJ/kg, respectively. Thus, the energy balance of the proposed process is overwhelmingly positive. A portion of the heat released during the combustion of the polymer pyrolyzates may be fed back to the pyrolyzer through a heat exchanger to gasify incoming precursors, whereas the remaining heat may be used elsewhere as process-heat or to generate electricity (see Appendix A1). Regarding the environmental impact of this process, it should be stated that the use of premixed flames, high temperature filtration, and possibly a post process afterburner can drastically reduce unburned or partially burned health-hazardous species, as shown before in this laboratory.25–32 Finally, emissions of the greenhouse gas CO₂ are not an issue when the “carbon-neutral” waste biomasses are used as feedstocks. [“If carbon reductions are equivalent to the total carbon footprint of an activity, then the activity is said to be “carbon neutral.” Quoted from http://www.britannica.com/EBchecked/topic/1585223/carbonoffset.] CO₂ appears to be an issue when waste tires or waste plastics are used as feedstocks. However, by using such waste hydrocarbons,
the conventionally used, more valuable premium hydrocarbons are merely substituted, and thus, 
CO₂ emissions (that would have been possibly released during their extraction and production) 
are avoided. In addition, there are also benefits to cleaning the earth of nonbiodegradable wastes. 

Over the past 50 years, the total amount of municipal solid waste (MSW) generated in the U.S. 
alone has increased by 3-fold from 80 million to 250 million tons. In recent years, 12% of this 
total has been nonbiodegradable polymers (plastics), of which only 7% are recycled because of 
limited markets and limited consumer compliance. A further increase of recycling is not only 
desirable but essential in addressing the issues of (a) continuously decreasing available landfill 
space and (b) ubiquitous land and water pollution (consider for instance the Great Pacific 
Garbage Patch and the plastic accumulation in the North Atlantic Subtropical Gyre), mainly 
caused by nonbiodegradable wastes, such as plastics and rubbers. To spur interest in recycling 
and reuse of such polymers, new markets for recycled products are needed. In 2009, for instance, 
30 million tons of plastic waste was produced in the U.S. alone, and 7 million tons of tire waste 
was produced. As most polymers are mass-produced and low-priced, they are readily 
discarded after use, thereby creating a vast solid waste pollution issue. Recycling efforts in past 
years have partly alleviated this problem; however, as recycled plastics and rubber are devalued 
products, i.e., typically they cannot be used in their original applications, identifying markets for 
recycled products is problematic. Generating value-added products, such as CNMs, from 
recycled waste plastics is thought to enhance the motivation for recycling, lower the cost of the 
products, and in turn, help overcome the hurdles of their large-scale use in consumer and 
industrial applications.
Besides the ever-increasing amounts of waste polymers, there are also ever-increasing amounts of waste biomass. This is partly because biomass-derived fuels, such as bioethanol, have been recently viewed as renewable, clean-burning, and carbon neutral energy resources with the potential of replacing large amounts of petroleum-derived transportation fuels.37,38 Nowadays the demand for bioethanol production is rapidly increasing, and this also increases the volume of the associated waste residues that need disposal. Bioethanol is produced from common crops, mainly from sugar cane and corn. For instance, Brazil, a country accounting for 50% of the world exports of sugar and a leader in the production of ethanol from sugar cane, produced and consumed more than 630 million tons of sugar cane in 2009 and generated approximately 142 million tons of waste bagasse as a solid residue.39 Similarly, dried distiller grains with solubles (DDGS) is the dried residue remaining after the starch fraction of corn is fermented with selected yeasts and enzymes to produce bioethanol and carbon dioxide.40–42 The amount of DDGS produced in the U.S., a leader in the production of ethanol from corn, was about 32 million tons in 2009.43

**Table 8: Elemental chemical composition of the feedstock materials used in this work (in wt. %).**

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>O</th>
<th>K</th>
<th>H</th>
<th>S</th>
<th>N</th>
<th>P</th>
<th>Ca</th>
<th>Fe</th>
<th>Si</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDGS</td>
<td>48.2</td>
<td>17.8</td>
<td>7.5</td>
<td>7.5</td>
<td>6.7</td>
<td>3.7</td>
<td>3.2</td>
<td>0.6</td>
<td>0.5</td>
<td>0.3</td>
<td>3.9</td>
</tr>
<tr>
<td>Bagasse</td>
<td>50.5</td>
<td>17.5</td>
<td>4.1</td>
<td>6.7</td>
<td>1.7</td>
<td>0.3</td>
<td>0.5</td>
<td>2.7</td>
<td>4.8</td>
<td>7.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Tires</td>
<td>85.8</td>
<td>---</td>
<td>---</td>
<td>7.3</td>
<td>2.3</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>4.6</td>
</tr>
<tr>
<td>PE</td>
<td>85.6</td>
<td>---</td>
<td>---</td>
<td>14.4</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.0</td>
</tr>
<tr>
<td>PET</td>
<td>62.6</td>
<td>31.8</td>
<td>---</td>
<td>4.7</td>
<td>0.1</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.8</td>
</tr>
</tbody>
</table>
4.2 Experimental

The raw materials used in this study were as follows: (i) DDGS provided by a North American ethanol-producing company, used as-received with grain diameters of ca. 500 µm; (ii) sugar cane bagasse provided by a Brazilian ethanol producing company, received in fiber form and pulverized to particle sizes smaller than 500 µm using a household blender; (iii) waste tires obtained from a local source in the form of chips without steel belts; (iv) shreaddings of a postconsumer PE milk jug; and (v) shreaddings of a polyethylene terephthalate (PET) bottle. Figure 22 shows snapshots of the feedstocks as well as of the samples derived therefrom and used in this work. Table 8 lists the chemical composition of these materials. The catalyst used in this work consisted of mesh screens, made from AISI 304 stainless steel (i.e., an alloy mainly composed of 67% iron, 18–20% chromium, and 11% nickel). They were precleaned before usage by sonication in alcohol; 300 × 100 mm pieces were rolled in cylinders with 40 mm diameters and then were inserted in the second furnace.

Experiments were conducted in a laboratory-scale apparatus, as illustrated in Figure 23, consisting of two furnaces in series, separated by a gas mixing section, where N₂ or O₂ gases were introduced. The process for this waste-to-CNM generation consists of three steps. In the first step, batches of solid feedstocks (4 g of DDGS or bagasse samples; 1 g of PE, tire, or PET sample) were introduced into the first furnace (the pyrolysis reactor) under a flow of nitrogen carrier gas. Pyrolysis reactor temperatures were in the range of 600–1000 °C. In the second step, the feedstock pyrolyzates were channeled through a mixing venturi to the second furnace (the
synthesis reactor). Oxygen was introduced to the venturi empirically only in the cases of feedstocks with low oxygen to carbon ratios in their chemical structure, shown in Table 8. The pyrolyzates of tires, PE, and PET ignited and burned in luminous premixed and fuel-rich flames anchored at the exit of the venturi, whereas the pyrolyzates of DDGS and bagasse did not ignite. In the third step, the pyrolyzates or the partial oxidation effluents of the feedstocks entered the synthesis reactor where the rolled-up catalyst substrate was placed, with its axis positioned along the direction of the gas flow (Figure 23). Synthesis reactor temperatures were in the range of 600–1000 °C, as summarized in Table 9.

CO and CO₂ gases in the effluents were monitored in real time with online infrared analyzers (California Analytical Instruments Mode 200 with a lower detection limit of 0.01%). Light hydrocarbons (LHCs) and hydrogen generated during the experiments were monitored offline at the exit of the synthesis reactor. Gases were withdrawn at a rate of 0.5 mL min⁻¹, using glass syringes mounted on a dual syringe pump. Gas analysis was performed by gas chromatography (GC), with a HP 6890-series instrument, detecting gases with volumetric concentrations larger than 1 ppmv. This instrument was equipped with two parallel columns, one coupled to a flame ionization detector, the other to a thermal conductivity detector (GC-FID and GC-TCD). Control experiments in the absence of the catalyst substrate screens (i.e., without meshes) were also performed, and the composition of the generated gases was likewise analyzed. The experiments lasted roughly 1 min, and the materials grown on the 304 SS meshes were examined by both scanning electron microscopy (SEM), using a Hitachi S 4800 instrument, with an accelerating voltage of 3 kV and a working distance of 8 mm, and transmission electron microscopy (TEM),
using both a JEOL 1010 instrument with an accelerating voltage of 80 kV and a JEOL 2000 high resolution TEM (HRTEM) with an accelerating voltage of 200 kV.

Figure 22: Feedstocks pyrolyzed (from left to right): DDGS, sugar cane bagasse, waste tires, postconsumer HDPE, and postconsumer PET.
Figure 23: Experimental apparatus: three-stage laminar-flow, electrically heated, muffle furnace, used for the CNM synthesis. Zone 1: pyrolysis stage. Zone 2: combustion stage*. Zone 3: synthesis stage. (*) A flame was present within the combustion stage only when oxygen was added to the venturi.

4.3 Results

The CNMs grown on the stainless steel meshes were characterized by SEM, TEM, TGA, and Raman spectroscopy. CNMs from sugar cane bagasse and PET bottle feedstocks are shown in Figure 24, generated under pyrolysis and synthesis reactor temperatures, which achieved the highest quantities and the highest perceived qualities. These conditions have been denoted by boldface font in Table 9. Quantity and quality were assessed by visual examinations of the substrates under SEM, where quality refers to the uniformity of the CNM dimensions, a lack of visible condensed tars, and the extent of substrate coverage. During the experiments, the feedstocks of PE and PET plastics decomposed completely at the high temperatures of this study, leaving no residues in the sample-containing porcelain boats. Bagasse, DDGS, and tires gasified partially, leaving chars and ashes in the boats, which were discarded after each experiment. This study used fresh catalyst substrates in all experiments. However, a cursory investigation revealed that it was possible to reuse the stainless steel meshes as catalyst substrates in multiple
experiments to successfully generate CNMs, although the quality and quantity of the product has not been fully assessed yet. In those cases, the CNM yields were determined, by mass relative to the mass of carbon in the feedstock, and ranged from 1% (for tires) to 13% (for PE), which are in line with other processes reported in the literature.44 It should be mentioned here that CNM yields were not maximized in this process, inasmuch as the amounts of the inserted catalyst substrates were not maximized.

<table>
<thead>
<tr>
<th>Feedstocks Investigated</th>
<th>DDGS</th>
<th>Sugarcane Bagasse</th>
<th>Tires</th>
<th>Polyethylene</th>
<th>PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis reactor</td>
<td>600, <strong>1000</strong></td>
<td>600, <strong>1000</strong></td>
<td><strong>600</strong></td>
<td>600, <strong>800</strong></td>
<td><strong>600</strong></td>
</tr>
<tr>
<td>Synthesis reactor</td>
<td>600, 800, <strong>1000</strong></td>
<td>600, 800, <strong>1000</strong></td>
<td>600, 800, <strong>1000</strong></td>
<td>600, <strong>750</strong>, 900</td>
<td><strong>1000</strong></td>
</tr>
</tbody>
</table>
4.3.1 Microstructural analysis

4.3.1.1 Scanning Electron Microscopy Images

Scanning electron microscopy (SEM) was used to inspect the catalyst substrates in order to determine whether nanomaterials were formed. Figure 25 shows SEM images of synthesized materials from DDGS, sugar cane bagasse, tires, PE, and PET; columns A and B display two different magnifications. A high number density of entangled CNMs can be seen to cover the catalyst mesh in all cases.

![SEM images of CNMs](image)

**Figure 24:** SEM images of CNMs generated from (a) sugar cane bagasse and (b) PET polymer feedstocks.

Experiments that used corn-based DDGS as a feedstock, generated the sample illustrated in Figure 25(1-A) and (1-B), which show large populations of nanomaterials, completely covering the catalyst meshes. This sample was produced at process temperatures of 1000 °C for both the pyrolysis and synthesis reactors. As shown in Figure 25(1-A), the materials have twisted and
crooked forms with irregular shapes and rugged surfaces. These nanomaterials resemble ropes with widths of 100–200 nm. Figure 25(1-B), taken at a higher magnification, shows the structure of these nanomaterials.

Figure 25: SEM images taken at low magnification (A) and high magnification (B) of typical CNMs synthesized at optimum operation conditions using carbon feedstock from (1) waste DDGS, (2) waste sugar cane bagasse, (3) waste tires, (4) waste polyethylene, and (5) waste PET.
The SEM images of nanomaterials synthesized from sugar cane bagasse, Figures 25(2-A) and (2-B), show cylindrical nanomaterials covering the catalyst surfaces. This sample was produced at process temperatures of 1000 °C for both the pyrolysis and synthesis reactors. Figure 25(2-A) illustrates that the nanomaterials are in the form of well-separated, long (∼50 µm), straight, and smooth-surface cylinders, whereas Figure 25(2-B), taken at a higher magnification, shows that the fibers have diameters in the range of 20–80 nm.

The SEM images of nanomaterials synthesized from tires, Figures 25(3-A) and (3-B), exhibit upshots of nanomaterials originating from the surface of the catalyst substrate. This sample was produced at process temperatures of 1000 °C for both the pyrolysis and synthesis reactors. Produced materials were in the form of long and often entangled cylinders with lengths of about 40 µm and widths of about 100 nm.

The SEM images of nanomaterials synthesized from PE, Figure 25(4-A) and (4-B), reveal the existence of cylindrical structures grown on the surface of the catalyst substrate. The lengths of these structures were typically 1–5 µm, whereas the diameters were in the range of 15–84 nm. This sample was produced at process temperatures 800 and 750 °C for the pyrolysis and the synthesis reactor, respectively.
Figure 26: TEM images taken at low magnification (A) and high magnification (B) of typical CNMs synthesized at optimum operation conditions using carbon feedstock from (1) waste DDGS, (2) waste sugar cane bagasse, (3) waste tires, and (4) waste polyethylene.

The SEM images of nanomaterials synthesized from PET, Figure 25(5-A) and (5-B), reveal the existence of cylindrical structures grown on the surface of the substrate catalyst. The lengths of these structures were typically 20 µm, and the diameters were in the range of 50–200 nm. This
sample was produced at process temperatures of 600 and 1000 °C for the pyrolysis and the synthesis reactor, respectively.

4.3.1.2 Transmission Electron Microscopy Images

TEM was used for detailed structural analysis of the nanomaterials. The materials produced from DDGS and from sugar cane bagasse feedstocks, along with those produced from tires, PE, and PET feedstocks are shown in Figure 26. In this figure, images labeled A were obtained by conventional TEM, whereas images labeled B were obtained by high-resolution TEM (HRTEM). In the case of DDGS, see Figure 26(1-A) and (1-B), the TEM images show that carbon nanomaterials were produced in the form of rugged and dense rope-like structures (termed CNRs in this work). In the case of bagasse, see Figure 26(2-A) and (2-B), the TEM images show that the produced cylindrical materials have tubular forms, which are characteristic of CNTs. Both samples were produced at process temperatures of 1000 °C, for both the pyrolysis and synthesis reactors.

A typical TEM image of the materials produced from waste tires is shown in Figure 26(3-A), where braid-like long CNMs were evident; their widths were ca. 100 nm, in agreement with SEM observations. The HRTEM image, shown in Figure 26(3-B), reveals parallel wall structures. This sample was produced at process temperatures of 1000 °C for both the pyrolysis and synthesis reactors. The TEM image of samples synthesized from PE feedstocks shown in Figure 26(4-A) reveals that the cylinders detected in the SEM images have hollow tubular structures, which are characteristic of CNTs. HRTEM of the same sample, shown in Figure 26(4-B),
indicates the presence of parallel graphitic layers. This sample was produced at process temperatures of 800 and 750 °C for the pyrolysis and the synthesis reactor, respectively.

4.3.2 Raman Spectroscopy

With the help of Raman spectroscopy, information on the structure and properties of carbon nanomaterials can be obtained. Three major vibration modes are typically encountered when CNMs are examined using Raman spectroscopy: the G-band, the D-band, and the 2D-band. The G-band is a common resonance feature of the Raman spectra of graphitic materials as a result of stretching of the C–C bond, and its peak is usually at \( \sim 1582 \ \text{cm}^{-1} \). The D-band is another common feature, induced by the presence of sp3-hybridized carbon, and its peak is usually at \( \sim 1345 \ \text{cm}^{-1} \). The 2D-band, which is also denoted as G’, is a feature of a second-order twophonon process, and its peak is usually found in the range of 2500–2800 cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>( I_G/I_D )</th>
<th>( I_G/I_{2D} )</th>
<th>( I_D/I_{2D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste DDGS</td>
<td>0.89</td>
<td>1.64</td>
<td>1.70</td>
</tr>
<tr>
<td>Waste Bagasse</td>
<td>1.25</td>
<td>1.44</td>
<td>1.30</td>
</tr>
<tr>
<td>Waste Tires</td>
<td>0.79</td>
<td>1.61</td>
<td>2.03</td>
</tr>
<tr>
<td>Waste Polyethylene</td>
<td>0.89</td>
<td>3.73</td>
<td>4.21</td>
</tr>
<tr>
<td>Waste PET</td>
<td>0.83</td>
<td>1.43</td>
<td>1.71</td>
</tr>
</tbody>
</table>

In this study, CNMs synthesized from the various solid waste feedstocks exhibit strong peaks of the G-band, indicating the presence of graphitic carbon. In addition, there were peaks
corresponding to the 2D-band, indicating the presence of parallel graphitic layers. One more feature that the synthesized CNMs share is the presence of the D-band, which indicates either disordered structures or impurities. For comparison purposes, calculated ratios of intensities between G- and D-bands, G- and 2D-bands, as well as D- and 2D-bands were summarized in Table 10. It is evident that the nanomaterials synthesized from bagasse pyrolyzates generated the maximum \( I_G/I_D \) ratio, which suggests that these CNTs possess the highest quality with the least disordered structures and/or impurities. CNFs synthesized from the partial oxidation effluents of tire pyrolyzates feature the lowest \( I_G/I_D \) ratio, indicating relatively poor quality with lots of disordered structures and/or impurities. In terms of \( I_G/I_{2D} \) and \( I_D/I_{2D} \) ratios, CNTs synthesized from the partial oxidation effluents of PE pyrolyzates feature the highest values among others. As a consequence, these CNTs contain relatively fewer parallel graphitic layers than the nanomaterials (CNTs, CNFs, CNRs) from the other feedstocks. This could be attributed to the lower synthesis reactor temperature, 750 °C, in the case of PE (that condition produced the maximum CNT yield for that feedstock), in contrast to the synthesis temperature of 1000 °C that was implemented in the cases of the other feedstocks. Postproduction treatment of these CNMs at a higher temperature in an inert gas is expected to enhance their graphitization. With Raman spectroscopy, the quality of CNMs, in terms of the presence of graphitic carbon, and that of parallel graphitic layers, could be examined on the macroscale. Combined with visual examination (e.g., SEM and TEM), Raman spectroscopy can serve as a tool for assessing the quality of CNMs.47–50
4.3.3 Thermogravimetric Analysis
Thermogravimetric analysis (TGA) was applied to assess the amount of inorganic residues contained in the CNM products from the different feedstocks. By running TGA in air, typical residues were in the neighborhood of 5.5 wt % at 800 °C. It is also worth mentioning that all CNM samples experienced a two-step weight reduction. The weight of the samples first decreased rapidly at around 200 °C, with weight losses ranging between 20 and 50%. This weight loss may be attributed to the devolatilization and decomposition of possible tar-like deposits on CNMs. As the temperature increased further to 700 °C, the samples experienced a more gradual weight loss (amounting to 10%), and thereafter there was an additional rapid weight reduction, during which most of the carbon was oxidized, leaving the aforementioned residues behind. These TGA results indicate the presence of more than one carbon nanostructures in the CNMs, which is consistent with the Raman spectra. Further studies, such as those examining the electronic states of carbon using X-ray photoelectron spectroscopy, may be useful to resolve the constituents of CNM products in this study.

4.3.4 Composition of Carbon-Bearing Species
The gases entering the synthesis reactor (i.e., the products of sequential pyrolysis and partial oxidation processes of the solid wastes feedstocks) contained CO, CO₂, hydrocarbons, H₂, and H₂O as well as the inert carrier gas, nitrogen. Mole fractions of CO were typically in the range of 4–13% (see Table 11). CO₂ fractions were in the range of 3–10% (also see Table 11), whereas H₂ were typically in the range of 1–8%. Prominent measured light hydrocarbons (LHCs) included methane, ethylene, acetylene, benzene, and toluene, see Figure 27. Smaller amounts of
ethane, propylene, propyne, ethylacetylene, and ethylbenzene were also detected. It is notable that the composition of LHCs varied in the effluents of the different feedstocks, with biomass wastes generating the highest aliphatic component mole fractions, whereas PET generated the highest simple aromatic component mole fractions.

Table 11: Summation of Carbon Dioxide (CO₂), Carbon Monoxide (CO), and Hydrogen (H₂)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>without catalyst</td>
<td>with catalyst</td>
<td>without catalyst</td>
</tr>
<tr>
<td>bagasse</td>
<td>5.8%</td>
<td>5.8%</td>
<td>12.5%</td>
</tr>
<tr>
<td>DDGS</td>
<td>4.1%</td>
<td>3.7%</td>
<td>6.5%</td>
</tr>
<tr>
<td>tires</td>
<td>2.1%</td>
<td>4.9%</td>
<td>7.3%</td>
</tr>
<tr>
<td>PE</td>
<td>9.1%</td>
<td>9.6%</td>
<td>5.3%</td>
</tr>
<tr>
<td>PET</td>
<td>9.8%</td>
<td>8.8%</td>
<td>5.7%</td>
</tr>
</tbody>
</table>
More specifically, the effluents of DDGS and of bagasse were rich in methane as well as other light aliphatic compounds. The effluents of PE were predominantly rich in ethylene, propylene, and acetylene. The effluents of PET were principally rich in benzene and, to a lesser extent, in methane. The effluents of tires, under the conditions of their oxidative pyrolysis herein, were not particularly rich in any LHC species. Overall, the cumulative detected LHC mole fractions were as high as 10% in the case of PE and as low as 2% in the case of tires, under the conditions of this investigation. All of these carbon-bearing gases (HC, CO, CO₂) are potential donors to CNM growth. In fact, the presence of the catalyst mesh consistently reduced the partial pressures of hydrocarbon gases, whereas it consistently increased that of H₂, when CNMs formed (Figure 27). The detected unburned hydrocarbons, as well as the carbon monoxide and the hydrogen content of these pyrolysis (or partial-oxidation) effluents, may be valuable constituents of a syngas that can be burned, either as-is or enhanced with natural gas, as needed, to cogenerate power. In fact, the mole fractions of combustible gases (hydrocarbons, CO, and H₂) may be drastically enhanced if the amount of inert carrier gas is curtailed. That will be inconsequential to the process and will lower its operating cost. Combustion of the syngas under appropriate operating conditions can also destroy trace hazardous compounds therein, such as polycyclic aromatic hydrocarbons (PAH), as previous research in this laboratory has documented.25–32,52

4.4 Discussion

The feasibility of utilizing the above-mentioned solid wastes as feedstocks for CNM synthesis is related to the fact that those alternative feedstocks consist mostly of carbon, as listed in Table 8.
Figure 27: Prevalent hydrocarbon emission products from the pyrolysis/combustion effluents of different solid feedstocks, in the presence or the absence of a stainless steel catalyst substrate. The operating temperatures of the primary and secondary furnaces are those listed in Table 9 in boldfaced text.

The thermal decomposition products of these feedstocks, if transformed properly, may be converted into well-defined CNMs, such as graphene and/or CNTs.19,53 However, studies in this laboratory22 and elsewhere54 have revealed that the chemical structure and composition of carbon feedstock affects the composition of the pyrolyzate gases (Figure 27), which in turn affects the properties of carbon nanomaterials in terms of, for instance, structural architectures and dimensions, such as length and diameters. Indigenous inorganic elements present in the structure of the feedstocks, with the exception of waste plastics, may pose an issue when they are
used in the waste up-cycling processes. Minerals such as sulfur, phosphorus, and zinc are present in the feedstock materials of DDGS, sugar cane bagasse, and tires (Table 9).

Although the majority of these minerals may remain in the bottom of the pyrolysis reactor, as solid residuals upon release of the carbon bearing gases, it is entirely possible that some of them may vaporize and enrich the gaseous reaction streams. This is attributed to the high pyrolysis temperatures utilized in this study, i.e, $T_p = 600−1000$ °C, which are higher than the boiling points ($T_b$) of some of the minerals (e.g., $T_{b,S} = 445$ °C, $T_{b,P} = 280$ °C, $T_{b,Zn} = 906$ °C). These inorganic elements have been shown elsewhere to have individual effects on CNM formation.55-57

The issue of contaminants, which may be present in waste plastics and tires, should also be addressed here. First and foremost, a basic requirement for this process would be to use presorted and precleaned solid wastes as feedstocks. For instance, postconsumer plastics feedstocks should be sourced from recycling centers where plastics get presorted, washed, and pelletized. Preliminary work was conducted on the effect of variations in the purity of feedstocks, by using both virgin and postconsumer supplies of PE (the latter in the form of a shredded prewashed milk jug in the laboratory). As illustrated in Figure 28, the collected data showed that the as-synthesized CNTs had consistent dimensions and degrees of graphitization, as long as the operation conditions were kept the same. If, despite the washing, small amounts of organic contaminants are still present in the waste feedstocks, it may be reasonably expected that they would be destroyed in the high-temperature pyrolysis and partial oxidation encountered in the first stage of this process. If the presence of small amounts of inorganic contaminants in the
waste feedstocks was to pose a problem in the CNM synthesis, the temperature of the ceramic filter could be controlled separately to condense vaporized inorganic species therein, thereby preventing them from reaching the synthesis stage.

Figure 28: (a) CNMs from virgin HDPE pellets and (b) CNMs from prewashed milk jug.

The raw feedstock materials used in this study generated different amounts of products of pyrolysis and partial oxidation, which are the carbon-bearing gases needed for CNM growth. Therefore, it is necessary to optimize the operating conditions of the process in order to achieve desired CNMs with targeted properties through efficient conversions of solid wastes. Studies conducted herein examined the following parameters: the pyrolysis temperatures ($T_p$) and synthesis temperature ($T_s$). Experiments were conducted at various operating temperatures, $T_p$ and $T_s$. The results showed that the synthesis temperature is a determining parameter. In the cases of DDGS, bagasse, tires, and PET, the optimum synthesis temperature was $T_s = 1000 \, ^\circ\text{C}$,
whereas in the case of PE, the optimum temperature was $T_s = 750 \, ^\circ C$. The lower $T_s$ of PE could be attributed to the high mole fractions of ethylene and acetylene in the pyrolysis and partial oxidation effluents, as alkynes and alkenes were found to be key precursors for enhanced CNT growth.\textsuperscript{58–60} As shown in Figure 27, ethylene and acetylene components of PE effluents are the highest in this study. The fact that PE is the only feedstock examined in this study which is composed solely of carbon and hydrogen elements may also be relevant. The presence of additional indigenous elements in the remaining feedstocks, such as oxygen, P, S, and Zn may have led to different reaction environments.\textsuperscript{61}

The pyrolysis temperature ($T_p$) was found in this study to be of lesser importance to the effectiveness of CNM synthesis. However, $T_p$ was shown to be the key factor influencing CNM purity, i.e., the lack of condensed tars. At the lowest pyrolysis temperature in this study, $T_p = 600 \, ^\circ C$, tar-like impurities were present on the CNMs, with the exception of the case of PET. Higher pyrolysis temperatures were found to be more favorable, as they promoted higher gasification. The optimum pyrolysis for PE for maximizing the gas yield has been reported to be $800 \, ^\circ C$;\textsuperscript{62,63} hence that value was chosen herein. The pyrolysis temperature for PET was then chosen to be $T_p = 600 \, ^\circ C$, as suggested by Artetxe et al.\textsuperscript{64}

4.5 Conclusions

A process has been designed and developed to catalytically convert solid wastes into value-added products, such as carbon nanomaterials. CNMs were synthesized either from renewable, clean-burning, and carbon-neutral bioresources or from nonbiodegradable waste plastics and
tires. Carbon-bearing gases, generated either from pure pyrolysis or from pyrolysis and sequential partial oxidation of solid waste feedstocks, were utilized as carbon donors. The carbon content of these gases was catalytically converted into CNMs on stainless steel meshes. The typical feedstock mass to untreated CNM conversion ratios in this study, even without optimization, ranged from 1% (in case of tires) to as high as 13% (in the case of PE). Experimental results suggest that the types and structures of the resulting CNMs (CNTs, CNFs, CNRs) are determined by the feedstock type, through the disparate mixtures of carbon-bearing gases produced when the different feedstocks are pyrolyzed. They are also influenced by the pyrolysis and synthesis process temperatures. This approach addresses two pressing societal and industrial problems simultaneously: the disposal of wastes and the cost-effective generation of technologically important materials. Up-cycling waste solid materials to supply carbon feedstocks for CNM growth, as well as harvesting the cogenerated syngas, may provide a solution for sustainable nanomanufacturing.

4.6 Acknowledgements

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4.8 References


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CHAPTER FIVE

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5. Oxidative heat treatment of 316L stainless steel for effective catalytic growth of carbon nanotubes

Abstract

Substrates consisting of stainless steel (SS) type 316L have been typically considered as non-responsive to catalytic formation of multi-walled carbon nanotubes (MWCNTs) because of the protective chromium oxide layers on their surfaces. In current practices lengthy multi-step pretreatments are needed to break down these protective layers. This study oxidized 316L SS wire mesh in air, at 800°C, for time periods ranging from 1 minute to 20 minutes prior to its use as a substrate catalyst for MWCNT synthesis from pyrolyzate gases of polyethylene, i.e., a mixture of hydrocarbons and hydrogen. The shortest pretreatment of the substrate (1 min) produced the maximum yield of MWCNTs (0.0145g/g of catalyst) in these experiments, whereas longer pretreatments resulted in progressively lower yields. The 10 min pretreatment produced MWCNT forests vertically growing in planes perpendicular to the substrate surface (the periphery of the cylindrical wires of the mesh), 20 µm long and 21 nm in diameter on the average. Shorter (1 to 9 min) or longer (11-20 min) substrate heat treatments did not produce aligned MWCNTs at this temperature. Oxidative heat treatments of the substrate lengthier than 20 min did not produce any nanotubes. The results demonstrated an expedient and cost-effective method to activate the 316L SS substrate, and resulted in controllable MWCNT growth.

KEYWORDS: Multi-Wall Carbon Nanotubes, Catalyst, Heat Treatment, Stainless Steel, CNT Forests.
5.1 Introduction

Carbon nanotube (CNTs) generation and applications have been studied for more than two decades since their discovery.[1-3] With their commercialization entering into the growth phase of product life cycle, it is important to integrate CNT processing with existing manufacturing methods.[4, 5] Major expenditures in CNT production arise from the costs of the carbonaceous feedstocks (raw materials), the catalysts, and the necessary process power consumption; hence, efforts have been made to lower such costs. For instance, municipal and industrial waste plastics and process biomass residues have been proposed as low-cost feedstock alternatives, [6-13] and stainless steel (SS) screens or chips have been proposed as cost-effective dual purpose substrates and catalysts[14, 15]. SS contains transition metals (iron, nickel, etc.) which are well-documented to be effective catalysts for CNT growth[16-18]. For instance, type 304 SS is readily-available and reasonably-priced, its application as catalyst is of technological interest to CNT manufacturing.[6, 15] Besides, SS can be used in templates of various geometries (porous block,[19] wire cloth (mesh),[14] tubing,[20] plate,[21, 22] etc.), which facilitates applications where direct interaction between CNTs and conducting substrates are desirable,[15, 21, 23] as well as the applications where the architectures of templates can serve as the structures.[24, 25]
However, having a passive film of chromium oxide on its surface, SS does not readily react with gaseous hydrocarbons, which are common carbon growth agents for CNTs. This is why pretreatment of SS is usually necessary to breach its outer protection layer. Typically, acid etching,[26] extensive heat treatment (usually longer than 30 minutes)[14, 27] / calcination,[19] plasma treatment,[23] laser treatment,[14] or combination thereof need to be applied on SS before CNT growth commences. Although in some cases pre-treatment may not be required,[28] efficient growth of CNTs demands substrate processing steps. Without any pretreatment, type 316L stainless steel, unlike 304 SS, shows very limited reactivity to gaseous carbon growth agents.[28] The main difference in composition between 304 SS and 316 SS is that whereas the former steel does not contain molybdenum (Mo), the latter does (< 2-3 % Mo). The presence of molybdenum to 316 SS, in contrast to its absence in 304 SS, is well known to enhance the former steel’s resistance to chemical attack by corrosion and oxidation. Thus, it is hypothesized herein that the presence of molybdenum may also be responsible for the reduced reactivity of the 316
SS for CNT growth. Whereas, molybdenum has been reported elsewhere to exhibit catalytic activity for CNT growth, [29, 30] one may notice that such enhancements in catalytic activity have been reported only in the case where molybdenum was present together with cobalt (Co). Alvarez et al. reported that there is a synergistic effect between Co and Mo in the production of CNTs.[30] When both metals are simultaneously present, particularly when Mo is in excess, the catalyst is very effective. However, when they are separated they are either inactive (Mo alone) or unselective (Co alone).[30] Finally, in a recent study, Hordy and co-workers reported direct growth of MWCNTs from 316 stainless steels without any pretreatment,[31] however, during their furnace heat up (from room temperature to 700 °C) the stainless steel was held within the reactor, therefore some extent of heat treatment cannot be precluded in that study.

Vander Wal and Hall [14] suggested that upon the aforementioned surface treatments, fresh metal (majorly iron and nickel) underneath the chromium oxide layer become exposed to the environment, and serve as catalysts for CNT growth. Since most of long-lasting treatments are conducted at elevated temperatures and under oxidative conditions, metal grain particles grow to large sizes. An ensuing treatment, typically by passing through a hydrogen-containing gas at high temperature, [14, 20] is considered necessary to not only reduce the metal oxides into active metal catalysts but, also, to break the formed large grain particles and to create finer catalyst seeds facilitating the synthesis of CNTs. Consequently, CNT growth on stainless steel substrates largely depends on both their surface morphology and on their chemical composition; both of these factors affect the surface reactivity.
On one hand, numerous studies have been reported in the literature on the surface reactivity of stainless steels upon contacting oxidizing (or corrosive) environments, for the purpose of making their surface resistant to oxidation or corrosion. They have reported that thick passive layers and smooth surface features reduce the reactivity of such surfaces.[32, 33] Studies by Cho and co-workers concluded that high oxygen pressures lead to rough surfaces with distinct grains,[34] and that oxidation temperature and oxygen partial pressure are competing factors on the volumetric diffusion of chromium and the supply of oxygen.[35] They further revealed that a metastable oxide layer forms, containing significant amount of metallic chromium as well as excessive concentration of oxygen on top of the Cr$_2$O$_3$ layer at the initial stage of oxidation. [36]

On the other hand, very few, if any, studies have been reported on understanding the surface reactivity of stainless steels placed in contact with reducing environments, such as those required for CNT growth, where stainless steel surfaces experience streams of carbon monoxide, hydrocarbons, hydrogen, and/or mixtures thereof.

In this study, we demonstrated that brief heat treatments of 316L SS under oxidizing environments (such as air) are sufficient to allow subsequent growth of CNTs directly on their surfaces without the need of additional catalysts. Surface morphology tests, surface elemental analysis, and electrochemistry tests were utilized to shed light on the relationship between heat treatment time and nanotube fabrication through possible changes in surface reactivity. In fact, Our experiments were conducted in a two-stage reactor (described elsewhere)[8], where feedstock of solid post-consumer polymers (polyethylene, polystyrene, etc.) were pyrolytically gasified to supply gaseous hydrocarbons and hydrogen that are needed for the growth of CNTs.
5.2 Material and methods

5.2.1 Stainless steel heat treatment
Type 316L (AISI standard) stainless steel meshes (abbreviated as SS from now on unless explained otherwise), shown in Fig. 29, were used as both substrates and catalysts. They contained 16-18.5% Cr, 10-14% Ni, 2-3% Mo, <2% Mn, <1% Si, <0.045% P, <0.03% S <0.03% C, with the balance being Fe. The denomination L stands for low carbon content. Substrates were cut into pieces of either 1 cm × 3 cm, or 10 cm × 30 cm and were then rolled up. Samples were subsequently cleaned and rinsed using isopropanol in an ultrasonic bath for 10 minutes before being inserted into a quartz tube, preheated at 800 °C. Air was used as oxidation gas and no reduction reactions were followed. Oxidative heat treatments lasted for 1, 5, 10, or 20 minutes, separately, and the samples were then quickly removed from the hot area for cold air quenching. Longer duration heat treatments (e.g., 90 min) were also experimented with, but produced no CNTs. Experiments on the oxidative pre-treatment of SS substrates was repeated in triplicate.

5.2.2 Synthesis of carbon nanotubes
To achieve conversion of solid hydrocarbon fuels to CNTs, quantities of a solid feedstock, either post-consumer polyethylene or polystyrene, in pelletized form, were first thermally pyrolyzed into a stream of gaseous decomposition products (pyrolyzates) inside a pyrolyzer furnace at 600~800 °C. Pyrolysis occurred in inert nitrogen with a flowrate of 1 standard liter per minute (slpm), as this prevented the ignition and combustion of the pyrolyzates therein. The pyrolyzates then entered the second furnace where the aforementioned rolled up catalyst SS substrates were
pre-inserted. Growth of CNTs occurred on the catalyst substrates at a furnace temperature of 800 °C.

5.2.3 Characterization

Scanning electron microscopy (SEM, Hitachi S – 4800) equipped with energy dispersive spectroscopy (EDS) was used to reveal the surface morphology and elemental composition of the substrate, as well as of the synthesized CNTs. An accelerating voltage of 3 kV, a beam current of 10µA and a working distance of 8.2 mm were applied for SEM imaging, whereas an accelerating voltage of 30 kV, a beam current of 10µA and a working distance of 15 mm were applied for EDS analysis. Transmission electron microscopy (JEOL 1010) was used with an accelerating voltage of 70 kV and a beam current of 60 µA to examine the structure of the synthesized CNTs, CNTs were removed from SS meshes by sonication using 100% ethanol. When carbon nanotubes (CNTs) were identified, their cross-sectional diameters were determined by analyzing both SEM and TEM images with ImageJ, an image analysis software program maintained by the NIH. At least 200 individual tubes were measured at each condition. Statistical analysis was performed using Excel®.

Atomic force microscopy (AFM) was conducted using an Agilent 5500 instrument to analyze the steel substrate to investigate the substrate surface roughness down to the nanometer scale. AFM scanning was performed on the SS samples upon oxidation heat treatment of 1, 5, 10, or 20 minutes. An untreated steel sample was also investigated as a control sample. The samples were cut into 1 cm by 1 cm small pieces and were immobilized on glass cover slides using double-sided tape. Thin film topography was obtained by contact mode scanning, using a regular AFM
cantilever (CONTV-A, Bruker, Inc.). Scanning velocity was set at 1 line/second with resolution of 256 lines/frame. A typical topography was first identified with a low resolution scanning mode and, subsequently, 5 µm high-resolution scanning was implemented, upon repositioning the AFM tip over various segments of the sample. At least six (6) different spots were examined using the AFM contact mode scanning for each sample and at least five (5) different topographies were used to calculate the surface roughness of each image.

An Autolab PGSTAT 30 potentiostat (Metrohm USA, formerly Brinkman Instruments) was used for cyclic voltammetry measurements in a 3.56 % (by weight) sodium chloride solution, made by dissolving 34 g of reagent grade NaCl in 920 mL of distilled water. After different oxidative heat treatments, SS samples with dimensions of 8 mm×6.25 mm were exposed to the NaCl solution. Voltammetry was carried out at room temperature in a three-electrode cell. All potentials are referred to a Ag/AgCl reference electrode (212 mV vs. SHE), and anodic currents are shown as positive. All the measurements were collected after stable open circuit potentials ($E_{ocp}$) of the electrodes in the solution were achieved.

Thermogravimetric analysis (TGA) was conducted using a Q50, by TA, instrument. The heating rate was of 20°C•min⁻¹ under air flow.
Figure 30: SEM images of SS substrates after oxidizing heat treatment of a) 0 min, b) 1 min, c) 5 min, d) 10 min, e) 20 min, and f) 90 min. The scale bar represents 400 nm.
The temperature increased from \( \sim 25^\circ C \) to 900°C. Raman spectrometry was conducted using Jobin Yvon LabRam HR800 with 488nm wavelength laser probe, 100X objective, laser spot of \( \sim 1 \) \( \mu \)m and signal collection of 60 seconds.

5.3 Results and discussion

5.3.1 Effects of the heat treatment on the morphology and composition of substrate surface

The substrate surface is the parameter of outmost interest in this study as it is directly involved in CNT growth. Therein, the chromium forms a passivation layer of chromium oxide (Cr\(_2\)O\(_3\)) upon exposure to oxygen, imparting the appearance of a smooth and shiny surface (see Fig. 30-a). In contrast to this rather smooth surface of the untreated substrate (with its inherent grain boundaries,), particle islands appeared upon heat treatment for 1 minute (see Fig. 30-b). In this sample, the top surface layer formed cracks, which is consistent with reports elsewhere.[14]

Two types of surface morphology were evident, one with individual surface extrusions, and the other with bumps of larger coverage. However, although dome-like structures emerged as the treatment time increased to 20 minutes, each structure was rather smooth without clear borders. By contrast, individual surface extrusions with sharp edges and sizes around 200 nm are evident at prolonged heat treatments; for example a 90 minutes treatment (see Fig. 30-f). Further characterization using AFM reveals the effects of the heat treatment quantitatively. Representative AFM images (shown in the supplemental information Figures 38 and 39) illustrate similar trends in substrate surface development as seen in SEM images. Further
analysis using line scanning data (supplemental information Figure 40) enables the calculation of Root Mean Square (RMS) Roughness for each sample, through the following equation [37]:

\[ R_q = \sqrt{\frac{1}{L} \int_0^L (Z(x) - Z_0)^2 \, dx} \]

Whereas \( Z \) is the surface topography along the scan line, and \( Z_0 \) is the averaged surface topography, \( L \) is the total scanning length. Calculation results are listed in Table-12, showing that the RMS roughness started from 15±4 nm for surface without oxidative heat treatment, and this value increased to 44±6 nm for surface with 90 min oxidative heat treatment.

**Table 12: Surface RMS roughness for 316L stainless steels with different heat treatment duration.**

<table>
<thead>
<tr>
<th>Treatment Time (min)</th>
<th>RMS Roughness (nm)</th>
<th>RMS Roughness STD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0’</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>1’</td>
<td>26</td>
<td>6</td>
</tr>
<tr>
<td>5’</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td>10’</td>
<td>33</td>
<td>6</td>
</tr>
<tr>
<td>20’</td>
<td>34</td>
<td>6</td>
</tr>
<tr>
<td>90’</td>
<td>43</td>
<td>6</td>
</tr>
</tbody>
</table>

Besides the examination of the evolution of surface morphology with oxidative heat treatment duration, the surface chemical composition was also assessed by EDS analysis. As listed in Table 13, the major elements in the 316L stainless steel sample surface were thus determined. The mass concentration of Mo, Cr, Mn, Fe, Ni were in line with the 316L SS initial composition, and did not exhibit obvious changes upon heat treatment. The mass concentration of oxygen,
however, showed a remarkable increase, from 0.64 ±0.02% (at no heat treatment), to 1.03 ±0.03% (with a 1 minute heat treatment), and 1.35±0.05% (20 minutes heat treatment); such an increase is attributed to the surface oxidation at high temperature.

Table 13: Surface composition (by wt.%) of SS substrate before and after heat treatment

<table>
<thead>
<tr>
<th>Oxidative Heat Treatment - min</th>
<th>O (%)</th>
<th>Mo (%)</th>
<th>Cr (%)</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Ni (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.64±0.02</td>
<td>1.67±0.04</td>
<td>16.91±0.05</td>
<td>1.59±0.05</td>
<td>69.28±0.09</td>
<td>9.91±0.08</td>
</tr>
<tr>
<td>1</td>
<td>1.03±0.03</td>
<td>1.70±0.04</td>
<td>17.03±0.08</td>
<td>1.60±0.08</td>
<td>69.19±0.25</td>
<td>9.44±0.20</td>
</tr>
<tr>
<td>5</td>
<td>1.10±0.03</td>
<td>1.83±0.02</td>
<td>16.93±0.12</td>
<td>1.49±0.12</td>
<td>69.04±0.35</td>
<td>9.60±0.24</td>
</tr>
<tr>
<td>10</td>
<td>1.25±0.02</td>
<td>1.78±0.04</td>
<td>16.85±0.12</td>
<td>1.69±0.08</td>
<td>68.68±0.21</td>
<td>9.76±0.18</td>
</tr>
<tr>
<td>20</td>
<td>1.35±0.05</td>
<td>1.63±0.04</td>
<td>16.90±0.13</td>
<td>1.55±0.07</td>
<td>68.94±0.18</td>
<td>9.65±0.24</td>
</tr>
</tbody>
</table>
Figure 31: Comparison of cyclic voltammograms obtained for 316L SS substrates after different heat treatments in a NaCl solution, from -1.0 V to +0.2 V vs. Ag/AgCl at 50 mV s-1 scan rate.

5.3.2 Effects of the heat treatments on the reactivity of substrate surfaces

Potentiodynamic measurements showed that the cyclic voltammograms of all the heat treated SS meshes have similar shapes (Fig.31), but they are all different than that of the as-received SS mesh. The use of a potentiostat may help to elucidate the qualitative determination of a substrate’s reactivity. Specifically, a peak associated with reversible partial oxidation of iron oxide (-0.46 V vs. Ag/AgCl) [38] was only present in the case of the stainless steel surface without oxidative heat treatment, see Fig. 31. The disappearance of the reversible partial oxidation peak confirms that a higher oxidation state of iron has been reached on the SS surface upon high temperature oxidation. Besides, the peak associated with reversible partial reduction
of nickel oxide moved from (-0.69 V vs. Ag/AgCl) to (-0.81 V vs. Ag/AgCl) after heat treatment, see Fig.31.

Table-14 lists the parameters of open circuit potential (Eocp), pitting potential (Epit) and passive region, which were obtained from the voltammograms. Open circuit potential, Eocp, describes the potential of a sample relative to the reference electrode when no voltage or current is being applied. Pitting potential, Epit, signifies a potential threshold above which pitting (a localized reaction) grows but below which pitting ceases to occur. [39] Smaller Epit (-0.43<-0.27) indicates lower oxidation/corrosion resistance.[40] A larger passive region, ΔE = Eocp - Epit, indicates either thicker passive layers, or greater resistance to pitting.[41] The experimental data listed in Table 14 suggest that longer oxidative thermal treatments of SS substrates, thicken the passive layer, as indicated by a larger measured passive region (ΔE), and increase oxidation/corrosion resistance, therefore decrease the SS surface reactivity. This is consistent with the trend in CNT yields obtained herein, as described in an ensuing section. This is also consistent with results reported elsewhere.[42, 43] However, future study combining surface morphology, composition, electron states and crystal structures of the formed oxide thin film will be necessary to better understand the surface reactivity of 316L stainless steels in reducing conditions.
Table 14: Potentiodynamic measurements of SS substrates with lengthier oxidative heat treatments.

<table>
<thead>
<tr>
<th>SS heat treatment (min)</th>
<th>Open Circuit Potential, $E_{ocp}$ (V vs. Ag/AgCl)</th>
<th>Pitting Potential, $E_{pt}$ (V vs. Ag/AgCl)</th>
<th>Passive Region, $\Delta E$ (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.01</td>
<td>-0.436</td>
<td>0.446</td>
</tr>
<tr>
<td>1</td>
<td>0.10</td>
<td>-0.428</td>
<td>0.528</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
<td>-0.423</td>
<td>0.583</td>
</tr>
<tr>
<td>10</td>
<td>0.27</td>
<td>-0.322</td>
<td>0.592</td>
</tr>
<tr>
<td>20</td>
<td>0.32</td>
<td>-0.274</td>
<td>0.594</td>
</tr>
</tbody>
</table>

5.3.3 Effect of the substrate oxidative heat treatment on the growth of CNTs

Without any oxidative heat pretreatment, no CNTs formed on the 316L SS. Upon initial heat treatment under air, however, the entire surface of 316L SS was readily activated for the synthesis of CNTs, by breaking down its protective chromium oxide layer and exposing the metal underneath. Moreover, it was demonstrated for the first time, that subsequent reduction of 316L SS substrates is not necessary for efficient CNT growth.
Figure 32: Left column: SEM images of CNTs synthesized on the 316L SS substrates, with heat pretreatments of a) 1 min, b) 5 min, c) 10 min, and d) 20 min. Gaseous pyrolyzates of polyethylene were used as feedstocks. Both pyrolysis and synthesis reactor temperature were 800°C. Air was used as the pretreatment carrier gas with a flow rate of 1 slpm. Right column: CNT diameter distributions with mean diameter marked with blue lines.
Figure 33: Evolutions of type 316L SS substrate surface roughness, mean CNT diameter, and mean CNT yield versus heat treatment duration. Error bars are included in all plots, based on repeated measurements.
Table 15: Summary on surface roughness, CNT diameter and CNT yields upon different heat treatment duration.

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>RMS Roughness</th>
<th>RMS Roughness STD</th>
<th>Mean CNT Diameter</th>
<th>CNT diameter STD</th>
<th>Mean CNT Yield</th>
<th>CNT Yield STD</th>
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<tbody>
<tr>
<td>(min)</td>
<td>(nm)</td>
<td>(nm)</td>
<td>nm</td>
<td>nm</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>0'</td>
<td>15</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1'</td>
<td>26</td>
<td>6</td>
<td>27</td>
<td>7.7</td>
<td>1.45</td>
<td>0.37</td>
</tr>
<tr>
<td>5'</td>
<td>30</td>
<td>7</td>
<td>22</td>
<td>8.5</td>
<td>1.19</td>
<td>0.33</td>
</tr>
<tr>
<td>10'</td>
<td>33</td>
<td>6</td>
<td>20</td>
<td>9.3</td>
<td>0.73</td>
<td>0.26</td>
</tr>
<tr>
<td>20'</td>
<td>34</td>
<td>6</td>
<td>20</td>
<td>7.6</td>
<td>0.26</td>
<td>0.09</td>
</tr>
</tbody>
</table>

By comparison, most studies reported the need of lengthy treatments for the 316L SS under reducing atmospheres, in addition to those under oxidizing atmospheres.[44]

The heat treatment of SS and its effects on CNT growth, on the other hand, turned out to be tunable by simply varying the treatment durations. The yields as well as the dimensions of the resulting CNT products were readily controlled. Using the catalytic substrates of the SS meshes pretreated for 1, 5, 10, and 20 minutes, the mean diameters of the synthesized CNTs were 27±8.5, 22±8.5, 20±9.3, and 20±7.6 nm, respectively, see Fig. 32 and Table-15. Statistics suggested that the diameter variations closely fit the log-normal distribution, indicating there are several independent variables having multiplicative effects on the CNT diameters.[45] One way analysis of variance (ANOVA) suggests that heat treatments do affect the changes on surface roughness, CNT diameter and CNT yields (as shown in supplemental document).
As illustrated in Fig. 33, the mean yield (defined as the ratio of the mass of synthesized CNTs and that of the catalyst substrate) reached a maximum when SS meshes were heat treated for just 1 minute at 800 °C. Thereafter, the yield decreased with additional heat treatment time. There was no evidence of CNT generation when SS meshes were not pre-treated, or were pre-treated for 90 minutes, as shown in the supplemental information, Figure 41. Chernozatonskii and co-workers reported that the CNT diameter is affected by the catalyst particle size (grain),[46] which is further affected by particle mobility, sintering and re-dispersion processes. Such processes are generally represented by Ostwald ripening, [47], which describes phenomena occurring during continued heating of particles at the nanoscale.[48] As Ostwald ripening proceeds, the growth of larger particles and shrinking of smaller particles takes place and, eventually, the latter disappear via atomic inter-diffusion.[48-50] Therefore, the number of catalyst particles decreases while the average catalyst particle diameter increases, as also does the spread in the particle size distribution. Consequently, the decrease of CNT generation with substrate treatment duration yield may be partially due to a smaller number of catalyst particles suitable for CNT growth.

It is worth noticing that, longer oxidative heat treatment leads to not only larger catalyst particle sizes, see Fig. 30, but also to higher degrees of metal oxidation, which could block or poison the CNT synthesis.[14] This finding is consistent with those by Hofmann et al.,[51] who suggested that only crystalline metallic nanoparticles, not metal oxides, could serve as active catalysts; it also consistent with the findings of Nessim et al.,[52] who reported that catalysts with a high degree of metal oxides content were not effective in CNT growth. As indicated by the
distribution trends in Fig. 33, both the surface roughness (RRMS) and the CNTs’ diameters exhibited quadratic relations with the substrate oxidative pre-treatment durations (the trendline of the former being $y=-0.03x^2+1.1x+25$ with coefficient of determination $R^2=0.9997$ and the trendline of latter being $y=0.04x^2-1.3x+28$, with coefficient of determination $R^2=0.9401$, respectively). The mean CNT yields, however, exhibit a linear relation with heat treatment duration (the corresponding trendline being $y=-0.06x+1.5$, with coefficient of determination $R^2=0.9787$). Based on the results shown in Fig. 33, maximum roughness and minimum diameter (averaged) was achieved at heat treatments in the range of 10 to 20 minutes. Statistical analyses on the results of the parameters shown in Fig. 33 were conducted (a) for the surface roughness of the substrates based on 5 different topographies, (b) for the diameters of the CNTs based on 200 individual tube measurements, and (c) for yields, based on three different experiments. Error bars signifying standard deviation ($\sigma$) are shown in Fig. 33.
Figure 34: SEM images of MWCNT forests growing in planes laying vertical to the substrate surface (the periphery of the cylindrical wires of fine SS meshes (woven cloths). The SS were heat treated in air at 800 °C for 10 minutes prior to the MWCNT synthesis process. Subsequent MWCNT synthesis took place in pyrolyzate gases of solid polyethylene (1) or polystyrene (2) for a time of 1 min. Rows a, b and c show the MWCNT at progressively higher magnifications.

Besides the aforementioned changes on the dimensions, varying heat treatment durations turned out to affect the architectures of the synthesized CNTs. Although in most conditions, random
CNT clusters typically spread over the SS surface, vertically grown CNT forests were unexpectedly generated in planes perpendicular to the wire mesh catalyst surface (cylindrical wire periphery, as also illustrated in supplemental information, Figure 42), when the SS substrates were heat treated for 10 minutes before the carbon bearing gases were introduced to the synthesis reactor. As shown in Figs. 32c and 34, brush-like CNT arrays oriented vertically to the SS wire surfaces with a height of ~ 20 µm. It appears that the alignment of CNTs followed the striation of the drawing marks on the wires. TEM imaging of the resulting CNTs showed the absence of amorphous carbons (Fig, 35). However, the presence of non-crystalline structure of carbonaceous materials (such as CNTs with non-graphitized impurities) may not be excluded, as the corresponding oxidative thermogravimetric analysis (TGA) plot showed a slight decrease of mass around the temperature of 330 °C (Fig.36). As no complex pretreatments are needed, this result further supports the use of stainless steels as effective substrates for CNTs’ applications, especially for applications in electronics, where direct electrical contact is usually required between the CNTs and the substrates,[53] as well as in filtration, where templates are necessary to provide structural support of CNTs.[24, 25].
Figure 35: TEM image of CNTs with vertical alignment without any post treatment.

When CNTs are examined using Raman spectroscopy, the G-band, the D-band, and the G’-band are the three major vibration modes encountered, representing the corresponding structure and properties, see Fig. 37. The G-band with its peak at ~1582 cm$^{-1}$ is a common resonance feature of the Raman spectra of graphitic materials (sp$^2$ bonded carbon) as a result of stretching of the C–C bond.[54] With its peak at ~1345 cm$^{-1}$, the D-band is induced by the presence of sp$^3$-hybridized carbon. The G’-band, which is also denoted as 2D, has its peak usually found in the...
range of 2500-2800 cm$^{-1}$. It is a feature of a second-order two-phonon process.[54, 55] In this study, CNTs synthesized on the pre-treated SS mesh surfaces exhibit strong peaks of the G-band, indicating the presence of graphitic carbon.[56] In addition, there were peaks corresponding to the $G'$-band, indicating the presence of parallel graphitic layers.

![TGA plot of synthesized CNTs](image)

Figure 36: Representative TGA plot of synthesized CNTs. Reaction occurred in air at a heating rate of 20 °C/min.

It is worth mentioning that, surprisingly, in this study such vertically growing (and rather parallely-aligned) MWCNT forests could not be achieved with shorter or longer substrate pretreatment times. As shown in Figs. 32, when CNTs were grown on SS substrates treated for 1 minute, there was no evidence of vertical growth, even though the highest yields were achieved at that condition. Since vertical growth is usually considered as the result of the crowding
effect,[53] efforts have been made in this study to identify the possible contribution of heat treatment.

![Figure 37: Typical Raman spectrum of CNTs synthesized in this study](image)

Therefore, we propose that the vertical growth of CNTs is a result of the combined effects of optimized catalyst roughness and particle size, and consequentially nanotube diameters. This finding is also consistent with those by Robertson and co-workers,[57] who suggested that CNT alignment may be typically achieved by either increasing the packing fraction (such as increase in the catalyst particle density) or reducing the nanotube’s diameter.

In these experiments, concurrent substrate surface reduction of oxides and efficient CNT growth could be achieved since the polymer pyrolyzates, which were used as feedstocks, contain large
amounts of hydrocarbons and hydrogen. As costs associated with both etching and extra reduction treatments are thus eliminated, the treatment method reported herein has the potential for commercially-viable production scale-up.[4, 5]

5.4 Conclusions

In summary, it has been proven possible to activate the surface of the highly-corrosion resistant 316L Stainless Steel (SS) using brief oxidative heat treatments, in air at 800 °C. The steel was then used, in the form of fine wire screens (meshes), as both a substrate and a catalyst to generate multi-wall carbon nanotubes (MW-CNTs) in a reducing environment. Additional pretreatments such as etching and reduction of the SS were not necessary. Pyrolytic gasification of post-consumer polymers (plastics) of polyethylene and polystyrene (in nitrogen) was then used to generate a variety of gaseous hydrocarbons and hydrogen, which served as carbon donors to the CNT growth at 800 °C. Upon high temperature oxidative treatment, the smooth and shiny protective chromium oxide layer of the SS was destroyed and the catalyst surface roughness progressively increased to a maximum with the duration of the treatment. Upon exposure of the pre-treated SS substrates to the pyrolyzate gases in nitrogen, CNTs were readily formed and their diameters were found to decrease to a minimum with increasing substrate surface roughness. In the case where the catalyst substrate was pretreated for 10 min, MW-CNT forests grew vertically, along planes perpendicular to the substrate surface (the periphery of the cylindrical wires of the mesh). In all other cases MW-CNTs grew in all directions.
5.5 Acknowledgement

The authors thank Professor Kaitak Wan for use of AFM, Professor Sanjeev Mukerjee and Ms. Gizem Yilmaz for use of Potentiostat, Mr. William Fowle for use of TEM, and Professor Sagar Karmarthi for statistics analysis. Support from Department of Mechanical and Industrial Engineering at Northeastern University is acknowledged. C.Z acknowledges partial support from a Yamamura Fellowship.

5.6 References


[53] Y. Lan, Y. Wang, Z.F. Ren, Physics and applications of aligned carbon nanotubes, Advances in Physics, 60 (2011) 553-678.


5.7 Appendix 1

Figure 38: AFM images of SS substrates after oxidizing heat treatment of a) 0 min, b) 1 min, c) 5 min, d) 10 min, e) 20 min, and f) 90 min. Scan size: 5 × 5 µm.
Figure 39: AFM images of SS substrates after oxidizing heat treatment of 0, 1, 5, 10, 20 and 90 min. Scan size: 5 × 5 µm.
Figure 40: AFM line scanning data of SS substrates after oxidizing heat treatment of 0, 1, 5, 10, 20 and 90 min. Scan size: 5 × 5 µm.

Figure 41: SEM images showing no carbon nanotube were formed when SS meshes were not pre-treated (a), or were pre-treated for 90 minutes (b)
Figure 42: Left: CNT forests vertically growing on a flat substrate surface. Right: CNT forests vertically growing in planes perpendicular to a cylindrical substrate surface, i.e., the periphery of the cylindrical wires of the SS mesh.

Table 16: Surface Roughness One-way ANOVA-1 minute, 5 minutes, 10 minutes, 20 minutes

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<td>Groups</td>
</tr>
<tr>
<td>1 minute</td>
</tr>
<tr>
<td>5 minutes</td>
</tr>
<tr>
<td>10 minutes</td>
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<tr>
<td>Within Groups</td>
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<td>Total</td>
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Table 17: CNT Diameter One-way ANOVA- 1 minute, 5 minutes, 10 minutes, 20 minutes

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<tr>
<td>Groups</td>
<td>Count</td>
<td>Sum</td>
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<td>Variance</td>
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<tr>
<td>1 minute</td>
<td>231</td>
<td>6235</td>
<td>27</td>
<td>60</td>
</tr>
<tr>
<td>5 minutes</td>
<td>675</td>
<td>14513</td>
<td>22</td>
<td>72</td>
</tr>
<tr>
<td>10 minutes</td>
<td>903</td>
<td>18288</td>
<td>20</td>
<td>86</td>
</tr>
<tr>
<td>20 minutes</td>
<td>559</td>
<td>11102</td>
<td>20</td>
<td>57</td>
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<td>ANOVA</td>
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<td>Source of Variation</td>
<td>SS</td>
<td>df</td>
<td>MS</td>
<td>F</td>
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<tr>
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<td>9622</td>
<td>3</td>
<td>3207</td>
<td>44</td>
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<td>Within Groups</td>
<td>172168</td>
<td>2364</td>
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<td></td>
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<td>Total</td>
<td>181790</td>
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Table 18: CNT Yield One-way ANOVA - 1 minute, 5 minutes, 10 minutes, 20 minutes

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<th>Sum</th>
<th>Average</th>
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<td>4</td>
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<td>0.012</td>
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<td>10 minutes</td>
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<td>0.007</td>
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<td>20 minutes</td>
<td>4</td>
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</table>

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<th>df</th>
<th>MS</th>
<th>F</th>
<th>P-value</th>
<th>F crit</th>
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<td>0.00013</td>
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<td>Within Groups</td>
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<td>8.7E-06</td>
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<tr>
<td>Total</td>
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CHAPTER SIX

Manuscript under preparation
6. Effect of CO$_2$ Addition on Carbon Nanotube Formation from Thermal Decomposition of Ethylene

Abstract

Catalytic chemical vapor deposition (CVD) is a popular method to synthesize carbon nanotubes (CNTs). At the presence of catalysts (usually transition metals), the hydrocarbon feedstock decomposes controllably at elevated temperatures and can form tubular structures. It has been suggested that trace amounts of weak gas-phase oxidants, such as CO$_2$, can enhance the CNT synthesis by extending the catalyst life. It is not clear, however, how such additives affect the CVD reaction environment. In this study, ethylene gas was introduced to a preheated furnace/CVD reactor where meshes of stainless steel were placed. Therein ethylene was thermally decomposed in nitrogen mixed with different amounts of carbon dioxide. The meshes served as catalytic substrates for CNT growth. The compositions of the ethylene pyrolyzates were analysed both with and without the presence of catalysts, to explore the possible contributions of CO$_2$ addition to the CNT formation. The latter compositions were compared with kinetic model predictions of the thermal decomposition of ethylene. Both experimental and simulation results indicated that 1,3-butadiene (C$_4$H$_6$) was the most abundant hydrocarbon species of ethylene decomposition (at 800 °C) and that decomposition was inhibited at the presence of CO$_2$. A commensurate effect on CNT formation was observed experimentally, whereas the quality of CNTs got improved.
6.1 Introduction

Advanced materials, such as carbon nanomaterials (CNMs), are building blocks or additives to a variety of materials of technological interest. The global production of CNTs is currently 3,500 tons, with a projected annual production growth rate of 30.6%[1]. The global CNTs industry turned over around $668.3 million (in terms of production value) in 2010, and is forecast to grow to $1.1 billion by 2016 at a rate of 10.5%[2]. Expanding markets for their large volume applications[3], place ever-increasing demands on lowering their production costs. Current technologies for CNT production require intensive consumption of premium feedstocks and, often, of costly catalysts; they also require input of external energy [4].

Although CVD is a facile method for quality control and easy up-scale of CNT growth, its optimum conditions are usually derived from try-and-error, and varied from one system to another, depending largely on practical knowledge (the “Know-How”) [5-7]. For instance, whereas gaseous feedstocks supplied to CVD processes have been correlated to CNT products with proposed growth mechanisms[8-14], these feedstocks in fact could pyrolyze at the high reaction temperatures implemented therein (>400 °C) [15-20]. Therefore, the CNT substrate catalysts therein have likely experienced a blend of carbon-bearing gases, which are likely very different from the input feedstocks. Simply building a connection between the initial feedstocks and the CNM products is not sufficient. For instance, studies conducted in this laboratory synthesized CNTs using solid hydrocarbon feedstocks (plastics, biomass, tires, etc.) through sequential pyrolysis and combustion processes.[21-26] Solid feedstocks were first thermally
decomposed before being mixed with air (or oxygen-containing gases) to form a fuel-rich flame. The effluents reaching the catalysts were mixtures of unburnt hydrocarbons, carbon monoxide, carbon dioxide, hydrocarbon, water vapor, etc. The corresponding reaction schemes therefore become much more complicated.

When the effluents after the CNT formation were finally burned, the result is a gas stream consisting mainly of CO\textsubscript{2} and water, with minor amounts of oxygen, CO and pollutants. After condensing the steam and removing contaminants, such combustion stream is ready for replacing the expensive N\textsubscript{2} as the carrier gas. Such a replacing process can also been called exhaust gas recirculation (EGR).[27] The amount of recycled flue gas, especially the different CO\textsubscript{2} levels, is therefore an important parameter.

Table 19: Representative Synthesis Recipes of CNT Synthesis Using CO\textsubscript{2} as Additives

<table>
<thead>
<tr>
<th>Authors, Year &amp; Reference</th>
<th>Carbon Feedstock (flowrate, in ml/min)</th>
<th>Catalyst / Support</th>
<th>Temperature (°C)</th>
<th>Reaction Duration</th>
<th>Mole Fraction Ratios Between CO\textsubscript{2} / Carbon Feedstock</th>
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<tr>
<td>Magrez, et al., 2007, 2010</td>
<td>C\textsubscript{2}H\textsubscript{2} (8, 16)</td>
<td>Fe\textsubscript{2}Co/(CaCO\textsubscript{3}, MgO, Al\textsubscript{2}O\textsubscript{3}, TiN, SiC, TaB\textsubscript{7}, Nb\textsubscript{2}O\textsubscript{5})</td>
<td>400~820</td>
<td>15~30’</td>
<td>1</td>
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<tr>
<td>Authors</td>
<td>Methane (mol%)</td>
<td>Catalyst Composition</td>
<td>Temperature</td>
<td>Time</td>
<td>Product Distribution</td>
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<td>----------------</td>
<td>----------------------</td>
<td>-------------</td>
<td>------</td>
<td>---------------------</td>
</tr>
<tr>
<td>Li et al., 2008</td>
<td>CH₄ (50)</td>
<td>Fe/Mo/MgO (1:1:40)</td>
<td>900, 30'</td>
<td>0-0.5</td>
<td></td>
</tr>
<tr>
<td>Wei et al., 2009</td>
<td>Ar:H₂:C₂H₄:CO₂=250:200:100:X</td>
<td>Al₂O₃ (10.0 nm), Fe (1.0 nm), and MgO (1.0 nm) sequentially on a silicon wafer with SiO₂ of 600 nm thickness</td>
<td>730, 750, 770, 790</td>
<td>0, 0.068, 0.127, 0.225, 0.304, 0.368 (in total mol%)</td>
<td></td>
</tr>
<tr>
<td>Sels et al., 2011</td>
<td>CH₄ (50)</td>
<td>Ni(25 wt%)MgAl₂O</td>
<td>600</td>
<td>1</td>
<td></td>
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<tr>
<td>Sels et al., 2012</td>
<td>CH₄ (50)</td>
<td>Ni(x wt%)XTiO₃</td>
<td>700</td>
<td>3 hours</td>
<td>0, 0.5, 1, 2, ∞</td>
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</table>
It had been suggested that trace amount of weak oxidants, such as CO$_2$, can enhance the CNT synthesis by extending the catalyst life[28], preventing the formation of amorphous carbon[29], and by reducing the number of walls of the CNTs[30]. It is not clear, however, how these additives affect the CVD reaction environment. Most studies involving CO$_2$ as synthesis enhancer had utilized either alkane (CH$_4$)[29-32], alkene (C$_2$H$_4$)[28, 33], alkyne (C$_2$H$_2$)[34-36] or synthetic (CO and H$_2$ mixture)[37] fuels. Key operating parameters in these studies are summarized, in Table-19. For a typical lab scale reactor (with diameter in the order of several inches (0.01 ~ 0.05), and length in the order of several feet (0.3 ~ 1 m)), feeding rates are usually around or smaller than 1 liter/minute (lpm). The partial pressures of carbon feedstocks, i.e., light hydrocarbons, are normally the minority, while the rest are made up by inert carrier gas, as well as the additives. Typical reaction temperatures are between 600-1200 °C. Reverse Boudouard reaction and reverse water gas shift reaction have been indicated as possible steps governing the overall reaction, while the inside reaction pathways involving radicals are yet to be explored.[28, 38]

In order to account for the reality that there will be a blend of carbon-bearing gases at the location where CNT synthesis occurs (usually in the middle of the furnace), a kinetic model is applied in this study to reveal local gaseous reaction conditions along the reactor axis. Some of the kinetic calculation results will then be tested, compared, and validated with experimental results conducted in this laboratory. Since it is easier to first study a single fuel, rather than a mixture of the gaseous pyrolyzates of solid hydrocarbons, e.g., polyethylene, its major pyrolyzate, ethylene,[39-43] was chosen as the surrogate fuel in this study. Effects of different
CO₂ concentrations on the carbon decomposition and the gas products during ethylene CVD process will also be tested.

6.2 Experimental and simulation settings

6.2.1 Experiments
An atmosphere pressure CVD system was used in this study. It consists of a quartz tube, reactant gas supplies, and effluent gas analyzers. The overall layout is illustrated in Figure 43. The dimension of the quartz tube is 12 mm I.D × 600 mm, and is placed inside an electrically heated furnace with the effective heating zone of 300 mm. Four different reaction temperatures were studied: 984 K, 1033 K, 1081 K, and 1129K. The reactant gases were mixtures of ethylene, carbon dioxide, with the balance being nitrogen. They were fed to the reactor from gas cylinders through calibrated rotameter controllers. The total flow rate at 1081 K was 1000 mL/min (STP), resulting in a gas residence time of 0.528 s. This residence time was selected to be the baseline applied throughout this study. Total flow rates at 984 K, 1033 K and 1129 K were adjusted to 1099, 1046, and 957 mL/min, respectively, in order to achieve the same residence time.
Type 316L (AISI standard) stainless steel meshes (abbreviated as SS from now on unless explained otherwise), were used as both substrates and catalysts. They contained 16-18.5% Cr, 10-14% Ni, 2-3% Mo, <2% Mn, <1% Si, <0.045% P, <0.03% S <0.03% C, with the balance being Fe. The denomination L stands for low carbon content. Substrates were cut into pieces of either 1 cm × 3 cm, or 10 cm × 30 cm and were then rolled up. Samples were subsequently cleaned and rinsed using isopropanol in an ultrasonic bath for 10 minutes before being inserted into a quartz tube, preheated at 700 °C. Air was used as oxidation gas and no reduction reactions
were followed. Oxidative heat treatments lasted for 1 minute and the samples were then quickly removed from the hot area for cold air quenching. Such pre-treatment was applied in order to activate the catalyst surface, and to achieve maximum CNT yield.[21]

Table 20: Gaseous species identified from the ethylene fuel

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.0239%</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.0415%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>99.6846%</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.05%</td>
</tr>
<tr>
<td>CO</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

In the experiments, the reaction system is heated up to each reaction temperature in air before feeding the reactants (C₂H₄/CO₂/N₂). At each designated reaction temperature, the relative volumetric concentration of ethylene was kept constant (10%), while the concentration of CO₂ varied from 0%, 1%, 5%, 10%, and 20%, with the nitrogen balance adjusted accordingly. After a steady state, steady flow condition was achieved, a designated amount of catalysts were inserted quickly into the second half of the reactor, initializing the CVD reaction. The reaction lasted for 6 minutes, after which the reactor was purged by nitrogen while the sample was quickly removed.
from the reactor. Stainless steels were weighed both before and after CVD reaction to study the corresponding weight changes.

In each experiment, the outlet gas stream was withdrawn with syringes, mounted on a syringe pump; they were analyzed by gas chromatography (Agilent GC 6890A), using flame-ionization and thermal conductivity detectors (FID and TCD). The original ethylene feedstock was also examined to identify its purity, which is listed in Table-20. During the experiments, an on-line dual infrared analyzer (California Analytical Instrument, Model 200) was used to monitor the CO and CO$_2$ emissions. Scanning electron microscopy (SEM, Hitachi S – 4800) was used to reveal the surface morphology and elemental composition of the substrate, as well as of the formed carbon solids. An accelerating voltage of 3 kV, a beam current of 10µA and a working distance of 8.2 mm were applied for SEM imaging. Raman spectrometry was conducted using Jobin Yvon LabRam HR800 with 488nm wavelength laser probe, 100X objective, laser spot of ~1µm and signal collection of 60 seconds.

**6.2.2 Chemical kinetics simulation**

Computations, using a detailed chemical kinetics model while assuming a plug flow reaction were performed to not only compare with the experimental measurements, but also to investigate species that were not measured experimentally, such as H$_2$O and radicals. This model was developed by Howard and Richter, and has been shown in Ref. [44]. Its reaction mechanism includes 335 species and 8086 reactions. Pressure dependence of chemically activated reactions was addressed using Quantum Rice-Ramsperger-Kassel analysis [45], and corresponding rate constants were determined for atmospheric pressure conditions. The model was shown to be reasonably proficient at predicting concentrations of PAH and soot [44, 46-53]. Inputs to the
model were the chemical compositions of the reactants along with the nominal experimental temperatures.

The DSMOKE code was used to numerically solve the system of equations that describe various aspects of combustion in shock tube and ideal flow reactor [55]. This code includes multicomponent diffusion and thermal diffusion. Discretization of the differential equations is carried out using conventional finite differencing techniques for non-uniform mesh spacing. [54]

The numerical problem corresponds to a large system of differential-algebraic equations (DAE). The structure of this DAE system is a tridiagonal block, due to spatial discretization; most of the equations are devoted to the chemical species involved in the detailed kinetic scheme, with $(N_S + 4)$ equations for each discretization point, where $N_S$ is the number of species in the adopted kinetic scheme. The total number of equations is therefore equal to $(N_S + 4) \times N_P$, where $N_P$ indicates the number of points using for the numerical discretization in space. To handle the complexity of this problem, coupled to the intrinsic stiffness of the DAE systems [55, 56], a specifically developed C++ DAE class of the BzzMath library is adopted [57-60], aiming for the precision, robustness (because of high gradients and very different characteristic times of the chemistry of each species) and efficiency (reducing CPU time).

6.3 Results and discussions

6.3.1 Effects of CO$_2$ on the yield of formed solid matters

After CVD reaction, the mass of the stainless steel catalysts increased under all conditions. The mean yield is defined as the ratio of the mass increment and that of the catalyst substrate. In this study it reveals that the yield increased along with the increment of reaction temperature, as
illustrated in Fig. 44. This trend was consistent with the results reported elsewhere.[61, 62] For each designated temperature, it also reached a maximum when there were no CO$_2$ present in the reactants. Thereafter, the yield decreased with the addition of CO$_2$.

Figure 44: Results of yield analysis under different reaction temperature as well as different CO2 concentration.

Black matters appeared on the surface of stainless steel catalysts, while the detailed examination under SEM suggested that such matters possessed two types of morphologies: tubular and particles. As shown in Fig. 45, at the absence of CO$_2$ in the reactant stream, tubular structures appeared only at temperature settings of 984, 1033, and 1081 K. When CO$_2$ was introduced in the reactant stream, however, similar tendency could not be observed. At the lowest temperature, 984 K, the tubular structures appeared only when the concentration of CO$_2$ was 5%. It turned out
that under this concentration there were tubular structures at all the temperatures examined in this study. When the temperature increased to 1033 K, the tubular structures also appeared when 1% of CO₂ was added. When the temperature was set at 1081 K, tubular structures appeared throughout different CO₂ concentrations, although they were dominant only when the concentration of CO₂ was 5%. At the highest temperature of this study, 1129 K, tubular structures appeared only when the concentration of CO₂ was higher, or equal to 5%.

Figure 45: SEM images of condensed matters on the surface of stainless steel catalyst under different reaction conditions, scale bar: 1μm.
6.3.2 Effects of CO₂ on the quality of formed solid matters

Raman spectroscopy was also utilized to study the structures and properties of formed condensed matters. As the purpose of this study was to investigate the conditions for carbon nanotube formation, the conditions that resulted in tubular structures, as highlighted in Fig.45, were examined. There were the three major vibration modes encountered in the Raman spectra, namely G-band, the D-band, and the G’-band see Fig. 46. The G-band with its peak at ~1582 cm⁻¹ is a common resonance feature of the Raman spectra of graphitic material (sp2 bonded carbon) as a result of stretching of the C–C bond.[54] With its peak at ~1345 cm⁻¹, the D-band is induced by the presence of sp3-hybridized carbon. The G’-band, which is also denoted as 2D, has its peak usually found in the range of 2500-2800 cm⁻¹. It is a feature of a second-order two-phonon process. In this study, CNTs synthesized under 5% CO₂ environment exhibit strong peaks of the G-band, as shown in Fig. 46, indicating the presence of graphitic carbon. In addition, there were peaks corresponding to the G’2D-band, indicating the presence of parallel graphitic layers. Further analysis of Raman spectra revealed that the highest quality of CNTs in this study was achieved at 1081 K under the 5% CO₂ environment, as shown in Table-21.
Figure 46: Raman spectrum of tubular structures synthesized under 5% CO2 environment at different reaction temperature.
Table 21: Quantitative assessment of Raman spectrum analysis

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$I_G / I_D$</th>
<th>$I_G / I_{2D}$</th>
<th>$I_D / I_{2D}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>984</td>
<td>2.22</td>
<td>1.28</td>
<td>0.58</td>
</tr>
<tr>
<td>1033</td>
<td>2.52</td>
<td>1.45</td>
<td>0.58</td>
</tr>
<tr>
<td>1081</td>
<td>3.40</td>
<td>1.29</td>
<td>0.38</td>
</tr>
<tr>
<td>1123</td>
<td>2.63</td>
<td>1.35</td>
<td>0.51</td>
</tr>
</tbody>
</table>

6.3.3 Effluent gas species analysis: comparisons between experimental measurements and simulations without the presence of catalysts

With the reaction conditions examined for the CNT synthesis, efforts were also made to understand the addition of CO$_2$ on the gaseous species. Two CO$_2$ concentrations, 0% and 5%, were evaluated for the reaction occurred at 1081 K. First of all, simulation was conducted using the aforementioned Howard and Henning’s kinetics model, using the same inlet conditions applied in the experiments. Results of key species, namely C$_2$H$_4$, H$_2$, C$_2$H$_2$, C$_4$H$_6$, CO$_2$, and CO were summarized and plotted in Fig. 47. Gas chromatography was also applied to examine and compare the gaseous species at 1081 K. Both simulation and experiments showed clearly that, the ethylene feedstock readily decomposed, resulting in a mixture of hydrocarbon species, even
at such a short residence time (0.528s). Experiment results indicated higher ethylene decomposition, than what the kinetic modeling predicted. Higher concentrations of CH₄, C₂H₆, C₃H₆, C₂H₂, C₄H₆, C₇H₈, C₅H₈, and C₆H₆ were also suggested by the experimental measurements. Both experiment and the modeling suggested 1,3-butadiene (C₄H₆) be the most abundant hydrocarbon species of ethylene decomposition.

Figure 47: Comparison of GC measurements and simulation results for the reaction occurred at 1081 K, with 0% and 5% CO₂ addition, without catalysts.
What is more, when 5% CO$_2$ was present as additives, experiment and modeling suggested different results. In experiments, less decomposition of ethylene was found, whereas the simulations showed opposite results. Besides, in experiment there were more CH$_4$, C$_2$H$_6$, C$_3$H$_6$, C$_4$H$_6$, and C$_3$H$_8$ when 5% CO$_2$ was present, whereas there were less H$_2$, C$_2$H$_2$, C$_7$H$_8$ and C$_6$H$_6$. As a contrast, in simulation there were almost no changes for all the species after the addition of CO$_2$.

6.3.4 Effluent gas species analysis: comparisons on experimental measurements with and without the presence of catalysts

GC measurements of the gaseous species were also conducted with and without the presence of catalysts, in order to shed some lights on the possible carbon donors for the CNT growth. Experiments were also conducted, with catalysts, to include the CO$_2$ as additives. Without the addition of CO$_2$, the presence of the catalysts reduced the total amount of gaseous species, as shown in Fig. 48, due to the catalytic hydrocarbon decomposition reactions. Specifically, when CO$_2$ was not included in the reaction environment, the amount of C$_2$H$_4$ reduced, together with those of C$_3$H$_6$, C$_2$H$_2$, C$_4$H$_6$, C$_7$H$_8$, C$_3$H$_8$, and C$_6$H$_6$. Such reductions were accompanied by the increase of H$_2$, which is the byproducts of hydrocarbon decomposition, as well as by the CH$_4$ and C$_2$H$_6$.

With the addition of CO$_2$, on the other hand, the presence of the catalysts also reduced the total amount of gaseous species while increased the amount of H$_2$, however, to a lesser extent. Another difference with the CO$_2$ present was that amount of every identified hydrocarbon reduced without exemption.
Figure 48: Comparison of GC measurements for the reaction occurred at 1081 K, with 0% and 5% CO$_2$ addition, with and without catalysts.

It had been suggested that influence of inlet CO$_2$ could be attributed to the different reactions involving OH radicals[63-65]. As summarized in Table-22, reverse water gas shift reaction mechanism through OH radical, such as those in R6 ~ R11, could play an important role. Further study will be necessary to reveal the effect of catalyst presence.
Table 22: Suggested reaction themes involved in this study

<table>
<thead>
<tr>
<th>Reaction</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4 + \text{M} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2 + \text{M})</td>
<td>R1</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_4 + \text{M} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H} + \text{M})</td>
<td>R2</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_3 + \text{C}_2\text{H}_5)</td>
<td>R3</td>
</tr>
<tr>
<td>(\text{C}_3\text{H}_4 + \text{C}_2\text{H}_3 \rightleftharpoons 1,3\text{-C}_4\text{H}_6 + \text{H})</td>
<td>R4</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_3 + \text{M} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H} + \text{M})</td>
<td>R5</td>
</tr>
<tr>
<td>(\text{CO}_2 + \text{H} \rightleftharpoons \text{CO} + \text{OH})</td>
<td>R6</td>
</tr>
<tr>
<td>(\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O})</td>
<td>R7</td>
</tr>
<tr>
<td>(\text{H}_2 + \text{M} \rightleftharpoons 2\text{H} + \text{M})</td>
<td>R8</td>
</tr>
<tr>
<td>Chemical Reaction</td>
<td>Equation</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------</td>
</tr>
<tr>
<td>OH + H₂ ⇌ H₂O + H</td>
<td>R9</td>
</tr>
<tr>
<td>M + 2H ⇌ M + H₂</td>
<td>R10</td>
</tr>
<tr>
<td>CₙHₘ+(2n+m)OH ⇌ nCO+(m+n)H₂O</td>
<td>R11</td>
</tr>
</tbody>
</table>

### 6.4 Conclusions

In this study, ethylene was used as carbon feedstock to study the hydrocarbon thermal decomposition, with and without the presence of stainless steel based catalysts. CO₂ was used as additive to study its effects as a weak oxidant. The results confirmed that hot-wall reactor processes complicate the understanding of the synthesis process, as the inlet feedstock thermally decomposes and, thus, inevitably changes the composition of the carbon donor gases. Higher reaction temperatures lead to more carbon decompositions, whereas tubular structures were achieved only at certain reaction conditions. The addition of CO₂ showed inhibiting effects on the ethylene pyrolysis and CNT synthesis in this study, and further investigations are needed for a comprehensive understanding on the weak oxidants-involved reactions.

### 6.5 Acknowledgement

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Zhao. Chuanwei Zhao thanks Mr. William Fowle for SEM support and Mr. Fangze Liu for Raman spectra support.

6.6 References


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CHAPTER SEVEN
7. Conclusions

This dissertation studied both applied and fundamental aspects of upcycling municipal/industrial/agricultural wastes to value-added products, such as carbon nanomaterials and gaseous fuels.

Work of this dissertation has yielded the following results:

7.1 Up-cycling solid hydrocarbon wastes into carbon nanotubes (CNTs)

First and foremost, the following hypotheses were successfully validated:

(i) since pyrolytic gasification of waste plastics at around 800°C generates hydrogen and light hydrocarbons, the latter gases can then be used as carbon donor gases for CNT formation, while the former gas facilitates such formation, and

(ii) if pyrolytic gasification is followed by mixing of the gaseous pyrolyzates with oxygen to generate, upon ignition, a fuel-rich premixed flame, then the effluents of that flame can also be used as carbon donor gases and the flame itself can generate heat to sustain the CNT formation process.

The feasibility of generating CNTs, using sequential hybrid pyrolysis/CVD-synthesis or pyrolysis/premixed-combustion/CVD-synthesis processes, was proven. Gaseous hydrocarbons, hydrogen and CO were also generated as by-products of this process. A first-generation lab-scale experimental apparatus has been developed and tested to be a versatile platform to achieve the
aforementioned up-cycling conversion. Plastic wastes (of PE, PP, PS, or PETE), waste tires, sugarcane bagasse and DDGS were also proved to be effective carbon sources for CNT growth. These solid hydrocarbons were pyrolyzed in nitrogen at 600-1000 °C, and their optimized synthesis temperature range between 800 and 1000 °C. Stand-alone pyrolysis of solid hydrocarbons, or pyrolysis followed by premixed combustion of the resulting gaseous pyrolyzates generated gaseous carbon-donor agents for CNT growth on catalytic surfaces. In these processes, sufficient concentrations of carbon-containing species (either light hydrocarbons alone, or mixtures of light hydrocarbons, CO and CO₂), as well as diatomic hydrogen and water (in the latter case), were formed in situ safely and economically from the thermal treatment of the polymers. Utilizing a high-temperature ceramic barrier filter, process-generated particulates (soot) were removed prior to the CNT synthesis stage. In the case of the pyrolysis/combustion process, this feature allowed taking advantage of high fuel-to-oxygen ratios, as it prevented soot-contamination of the catalyst. CNTs were generated in time frames of 1 min, with typical lengths in the range of 1~20 μm, and mean diameters in the range of 20~85 nm; they were regular graphene-based, multi-walled CNTs. Parametric studies were performed to identify effective CNT generation conditions in terms of product yield, determined as the mass of the untreated CNT product to the mass of the feedstock material. The yields in this study, ranged from 1% (in case of tires) to as high as 13% (in the case of PE), which can increase further upon optimization.
7.2 Utilization of stainless steels as low cost catalysts for CNT synthesis

Type 304 stainless steel (SS) was first verified to be effective catalyst substrates for CNT synthesis, without the need of any pretreatment or additional catalysts. To the contrary, the surface of the highly-corrosion resistant 316L stainless steel (SS) needs activation. It was determined that brief oxidative heat treatments of 316L, in air at 800 °C, for time periods ranging from 1 minute to 20 minutes were necessary for subsequent CNT synthesis. The shortest pretreatment of the catalyst substrate (1 min) produced the maximum yield of CNTs per unit mass a catalyst ($0.0145 \text{g}_{\text{CNT}} / \text{g}$ of catalyst) in these experiments, whereas longer pretreatments resulted in progressively lower yields. The 10 min pretreatment produced CNT forests vertically growing in planes perpendicular to the substrate surface (the periphery of the cylindrical wires of the mesh), 20 µm long and 21 nm in diameter on the average. Shorter (1 to 9 min) or longer (11-20 min) substrate heat treatments did not produce aligned CNTs at this temperature. Oxidative heat treatments of the substrate lengthier than 20 min did not produced any nanotubes.

7.3 Effects of gas-phase additives (O$_2$ or CO$_2$) on the produced effluents and on the CNT synthesis

$O_2$ Addition When solid hydrocarbon wastes were used as feedstocks in batch processes, the effects of decreasing oxygen input to fuel-rich premixed flames on the synthesized CNT diameters were examined. The results showed that, as CO and CO$_2$ mole fractions increased, the CNT diameters decreased. A linear correlation was found between the concentrations of light aliphatic hydrocarbons in the flame effluents and the mean diameters of the resulting CNTs. A
similar correlation was shown between the product of the partial pressures of CO and H\textsubscript{2} and the mean diameter of the resulting CNTs.

\emph{CO\textsubscript{2} Addition} When ethylene was used as surrogate fuel for polyethylen pyrolyzates under steady-state steady-flow conditions, it was verified that ethylene readily decomposed under high temperature in a hot-wall CVD setting. Experiments showed that 1,3-butadiene (C\textsubscript{4}H\textsubscript{6}) was the most abundant hydrocarbon species of ethylene thermal decomposition at the presence of N\textsubscript{2} inert gas; this was supported by chemical kinetic calculations. Decomposition of ethylene was impeded at the presence of significant amounts of CO\textsubscript{2} (>1\%). At the presence of SS catalyst, the thermal decomposition of ethylene was enhanced, so was the consumption of its pyrolysis products, i.e., 1,3-butadiene (C\textsubscript{4}H\textsubscript{6}), acetylene, propene, benzene, toluene, and propane, as conversion to condensed matter took place on the substrates. The formation of carbon nanostructures also led to an increase of hydrogen formation. When CO\textsubscript{2} was added to nitrogen at a mole fraction of 5\%, the decomposition of ethylene was inhibited, and amount hydrogen was also curtailed but the partial pressure of 1,3-butadiene (C\textsubscript{4}H\textsubscript{6}) was slightly increased.

The addition of CO\textsubscript{2} in the range of 1vol\% to 20 vol\% was found to not only suppress the formation of solid carbons, but to also modify the types (morphology and structure) of the formed carbon nanostructures. Both experimental GC analysis and simulations suggested that the CO\textsubscript{2} altered the gaseous species inside the CVD reactor, which probably affect resulting condensed products.
CHAPTER EIGHT
8. Suggestions for Future Work

8.1 Engineering Applications

Exploration of the utilization of solid hydrocarbon waste mixtures, liquid hydrocarbon wastes and their mixtures, as carbon donors for CNT synthesis is suggested. Such mixtures better represent municipal/agriculture/industrial waste streams, as compared to those of individual hydrocarbon compounds.

The existing cold-wall reactor for CNT synthesis (see Appendix A2) can be improved to not only reduce the energy consumption, but to decouple the synthesis process from feedstock pyrolysis process, which is induced by the hot-wall reactor.

Existing external heating elements can be replaced by combustion-based heating, using a slip stream of the effluents from the aforementioned up-cycling process as energy input.

8.2 Fundamental Investigation

Reactivity investigation (electrochemical and analytical studies) of stainless steel surfaces in reducing gaseous environments will be helpful to better understand the reaction occur during the catalytic hydrocarbon decomposition. A fundamental understanding of CO₂ (or other additives, i.e., O₂, H₂O, etc.) on inhibiting, or promoting the synthesis of CNTs, where carbon 13 isotope could play a key role needs to be sought. For example, \(^{13}\text{CO}_2\) and / or \(^{13}\text{C}_4\text{H}_6\) with a predetermined amount of \(^{13}\text{C}\) will be mixed with ethylene (\(\text{C}_2\text{H}_4\)) and the mixture can serve as
carbon source for CNT formation. The resulting CNT sample can be examined using Raman spectroscopy [1-4] to determine whether the $^{13}$CO$_2$ (and/or $^{13}$C$_4$H$_6$) was a donor in the CNT synthesis. This knowledge will constitute a key building block in the understanding of the reaction scheme on the CO$_2$-enhanced CNT formation[5-8].

Last but not least, investigations can be made for a standard measure of the performance of different carbon-bearing species, in terms of their potential to effectively provide carbon atoms for CNT synthesis (similar to that of Octane Rating). With this regard, carbon activity (ac) may be a good dimensionless number to work with.

Carbon activity was initially used to quantitatively determine the tendency for graphite formation in metal corrosion studies. When metals are exposed to high temperature environments containing carbon-bearing gases, a specific corrosion, termed “metal dusting”, occurs and disintegrates the surfaces of alloy steels [9].

As illustrated in Fig. 49, for steels devoid of chromium[9], i.e., non stainless, rapid uptake of carbon into the metal leads to super-saturation and formation of metastable carbides (i.e., metal carburization). Ensuing decomposition of the carbides results in loosely adherent metallic particles, which can then act as catalysts for further carbon deposition. In metal dusting, therefore, a “buffer-type” layer typically refers to the dust, which is a powdery mixture of carbides, oxides, graphite and nano-sized metal particles. These metal nano-particles catalyze further deposition of carbon, from the gas phase [10-14], and catalyze the formation of carbon nanostructures.
The formation of SWNTs or MWNTs, on the other hand, is typically controlled by the predetermined catalysts. This is because particles, prepared either through coating or floating technology, are usually believed to serve directly as the “seeds” of CNT growth [15-31]. However, recent studies revealed that using certain catalyst configurations, delays were observed
before the launch of steady CNT synthesis. These catalysts were carburized, and underwent a
“self-organization” [32] or “rearrangement” [33] process. It was found that such process
typically came with a “buffer-like” layer, which was suggested to contain the final form of the
catalyst for CNT growth. In this latter case, the pre-determined catalyst particles, served
indirectly as the “seeds” for CNT growth. It is now understood that such carburization and
sequential “self-organization” steps are features of metal dusting [9, 34-44]. Metal dusting,
however, had not been paid attention in regards to its catalytic effects on mass production of
CNTs until recently [14, 44-48].

In the particular case of stainless steels (which is defined as steel alloys with a minimum of 10.5
or 11% chromium content by mass), the feasibility of synthesizing carbon nanostructures,
ranging from carbon nanorods, MWNTs, SWNTs, and nanoballs, from metal dusting of 304
stainless steels was explored by Chang et al. [46, 47]. Chang et al. [46] summarized Grabke’s [9]
reaction mechanism of metal dusting, in stainless steels, as follows: “(i) Carbon is transferred
from the carbon-supersaturated environment to the steel surface through local defects (induced
by sand-blasting or other means) in the oxide film and dissolves in the steel. (ii) The dissolved
carbon diffuses inward and causes internal precipitation of stable carbide, M_{23}C_6 and/or M_{7}C_{3},
where M consists mainly of chromium (Cr). (iii) Upon further carbon transfer, metastable
carbide, M_3C forms on the internal carbide (where M consists mainly of iron (Fe)). (iv) Due to
the low carbon diffusivity in M_3C, graphite nucleates and grows on the sample surface upon
carbon deposition. (v) The decomposition of M_3C is triggered by graphite deposition, which
decreases the carbon activity at the M_3C/graphite interface to unity. The carbon atoms attach to
the basal planes of the deposited graphite, which grows into the sample surface; the metal atoms diffuse outward through the graphite layers and agglomerate to nanosized particles. (vi) These metallic nanoparticles act as catalysts for formation and growth of nanosized carbon materials. Further carbon deposition from the atmosphere makes the above steps repeat indefinitely.”

Metal dusting occurs in strongly carburizing environments, when the gas is supersaturated with respect to carbon. At temperatures in the range of 400-800 °C, gas-phase reactions of carbon-bearing gases around metal surface have been proposed [9, 49] as shown below in Table 23. The parameter carbon activity, $a_C$, listed therein is used to quantitatively determine the tendency for graphite formation.

### Table 23: Summary of Proposed Gas Phase Reactions and the Corresponding Carbon Activities

<table>
<thead>
<tr>
<th>Reaction Scheme</th>
<th>Carbon Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{C}$</td>
<td>$a_{C,1} = \frac{K_1 \cdot P_{\text{CO}} \cdot P_{\text{H}<em>2}}{P</em>{\text{H}_2\text{O}}}$</td>
</tr>
<tr>
<td>$2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$</td>
<td>$a_{C,2} = \frac{K_2 \cdot (P_{\text{CO}})^2}{P_{\text{CO}_2}}$</td>
</tr>
<tr>
<td>$\text{C}_x\text{H}_y \rightleftharpoons \frac{y}{2}\text{H}_2 + x \text{ C}$</td>
<td>$a_{C,3} = \left(\frac{K_3 \cdot P_{\text{C}_x\text{H}<em>y}}{(P</em>{\text{H}_2})^{y/2}}\right)^{1/x}$</td>
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Where $P(CO)$, $P(H_2)$, $P(H_2O)$, $P(CO_2)$, and $P(C_xH_y)$ are the partial pressures of CO, H$_2$, water vapor, CO$_2$, and hydrocarbons, respectively, and $K$ are the equilibrium constants of the forward reactions. $a_C = 1$ when the atmosphere is in equilibrium with graphite [49]. The carbon deposition occurs when the carbon activity, $a_C > 1$. This carbon activity is a thermodynamic variable, depending on the partial pressures of participating gases and on the reaction temperature. Regarding the partial pressure dependence, previous studies investigated the effects of gas components on the metal dusting process in iron [50]. For example, various CO/H$_2$/H$_2$O gas mixtures had been examined at a reaction temperature of 700 °C. With $a_C$ as an indicator, the carbon take-up was found to increase with increasing CO partial pressure, and reached a maximum at 60–75 vol% of CO.

With the $a_C$ as an indicator on hand, it may be useful to examine existing synthesis environments for CNT growth. Suitable ranges of carbon take-up for optimizing CNT synthesis may therefore be revealed.

8.3 References


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APPENDIX 1

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A1. Pyrolytic Gasification of Post-Consumer Polyolefins to Allow for “Clean” Premixed Combustion

Abstract

Utilization of post-consumer waste plastics as fuels is of technological interest since their energy contents (heating values) are comparable to those of premium fuels. Pyrolytic gasification of these solid polymers yields a mixture of predominately gaseous hydrocarbons and hydrogen. This gaseous fuel mixture can then be suitably blended with air and burned in well-controlled premixed flames. Such flames are much less polluting than diffusion flames, which would have been generated had the polymers been burned in their solid state. In this work an apparatus was designed and built to continuously process polymers, in pelletized form, and to pyrolytically gasify them at temperatures in the range of 800-900 °C in N₂ or CO₂-containing environments. Subsequently, the gaseous pyrolyzates were mixed with air, ignited and burned in a Bunsen-type burner in a manner similar to natural gas. Polyethylene and polypropylene pyrolyzates burned with blue-tint flames akin to those of natural gas. The flames were fairly-steady and nearly-stoichiometric, generating effluents with low CO/CO₂ ratios. The combustion reactions released heat in a small water boiler coupled to a miniature steam engine, which produced electricity illustrating the feasibility of “clean” power generation from waste plastics. As pyrolysis of polyolefins requires a nominal heat input that amounts to only a minuscule fraction of the heat released during their combustion, large-scale implementation of this technique is deemed to be indirect combustion technique was followed in this work, which called for a two-step process:
pyrolytic gasification of the solid polymers, followed by premixed combustion of the gaseous pyrolyzates with air. Such conditions afford effective mixing of gaseous fuel compounds with oxygen and can generate low emissions of pollutants. In fact, Goncalves et al. reported that indirect homogeneous combustion of PE pyrolyzates released 10 times lower polycyclic aromatic hydrocarbons (PAH) and particulates than direct combustion of the same polymer, at similar furnace operating conditions.

Indirect combustion of the plastics (pyrolytic gasification followed by combustion of the pyrolyzate gases) is technically attractive, as Jinno et al. reported values for the heat of pyrolysis of PE and that of PP that are well-under 1 MJ/kg. Even after accounting for the higher temperatures encountered in pyrolytic gasification herein than those in the aforementioned work, the heat of pyrolysis of polyolefins is in the range of 1.8-2.4 MJ/kg. Comparing this value to the heating values (energy contents) of polyolefins, which are in range of 44 - 46 MJ/kg, it becomes evident that only a small fraction of the heat released during combustion will be needed to be fed back to pyrolytically gasify them. Therefore, a gaseous fuel stream may be produced from waste polymeric feedstocks by implementing a heat integration, where only a small penalty in energy, and thus in the operating cost of a power plant, will be encountered in running the gasifier. Based on this principle, this study developed and tested a process that accepts post-consumer plastics and releases their internal energy through environmentally-benign indirect combustion. The feasibility of this process has been proven using polyolefins, the most voluminous commercial plastics.
Polyolefins is the collective description for plastics types that include polyethylene - low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and high density polyethylene (HDPE) - and polypropylene (PP). Polyolefins are polymers produced from simple olefins (also called alkenes with the general formula $\text{C}_n\text{H}_{2n}$) as monomers. Because of their versatility, low cost, inertness and excellent chemical resistance, polyolefins are the most popular plastics in use today. Together they account for nearly half of Europe’s total generation of 24 million tones and USA’s generation of 30 million tons of all plastics each year$^1$. Polyethylene (PE), either as high-density (HDPE) or low-density (LDPE), starts decomposing at 290°C by scission of weak links and progressively by scission of tertiary carbon bonds or ordinary carbon bonds in the beta position to tertiary carbons$^8$. Extensive weight loss is not observed until 370°C is reached. The main products of its decomposition are: an oil/wax product dominated by alkenes, alkynes, and alkadienes; a gas consisting mainly of alkanes and alkenes; and negligible char$^4, 9$. The monomer precursor ethylene (ethene) is only one of many constituents of the volatile primary products. For instance, there is also formation of aromatic species such as benzene and toluene. As the temperature of pyrolysis increases, gaseous products are favored. Extensive work by Conesa and co-workers$^{10}$ examined the effects of the polyethylene type, the effects of polymer branching, the effects of batch versus continuous operation, as well as the effects of the influence of the heating rate on the decomposition yields. They found variations in both the yields and the composition of the pyrolyzates, with branched PE yielding 91.8% gas with a higher aromatic content, and less branched PE yielding 97.5% gas with lower aromatic content, both at 800°C. These results are in good agreement with those of
Scott et al. and Kaminsky. Westerhout et al. found that, at 800°C, the product contains more methane than ethylene and low amounts of aromatics and, most importantly, they determined that the type of pyrolyzed PE, i.e., LDPE or HDPE, had no significant influence on the product spectrum produced. The effect of the residence time and the temperature of pyrolysis on the products distribution were studied by Mastral et al. in two free-fall reactors, placed in series. Their experiments showed that up to 700°C the main products obtained were waxes and oil fractions; and that the gas yield increased as the temperature increased. The generation of aromatics was reported to be significant at 800°C and showed an increasing trend with temperature and residence time. The main compounds present in the gas fraction were hydrogen, methane and acetylene at temperatures up to 1000°C. Longer residence times led to a more intense cracking of the aliphatic fractions, and the methane and ethylene yields increased significantly. Lee et al. reported on the oxidative gasification of mixed plastics in a 500 KW_th pilot scale system including a flame-assisted tar reformer and a sequential gas cleaning processes. The cleaned producer gas, was composed mainly of hydrogen, carbon monoxide, carbon dioxide and methane.

Polypropylene (PP), having every other carbon in the main chain as a tertiary carbon is prone to attack; this lowers the stability of PP as compared to PE. Polypropylene starts decomposing at 230°C by chain scission and chain transfer reactions; volatilization becomes significant above 300°C. High temperature pyrolysis of PE and PP has been reported in the literature to generate a mix of light hydrocarbon gases, including methane, ethylene, propylene, butylene, etc. and hydrogen.
This experimental study aims at demonstrating that a high-energy-content gaseous fuel can be produced from post-consumer polyolefin feedstocks and can be burned in an environmentally-benign manner, akin to natural gas, for power generation, process heat or other energy-related applications. A laboratory-scale system was designed and constructed to pyrolytically gasify peletized polymers, at steady-state steady-flow conditions, and to generate a combustible gaseous fuel and burn it in a miniature steam engine to generate electricity. Pyrolytic gasification took place in both N\textsubscript{2} and CO\textsubscript{2} carrier gases. The reason for comparing these two background gases because whereas N\textsubscript{2} has to be purposely procured from a cryogenic air separation plant, and is thus costly, a mixture of N\textsubscript{2} and CO\textsubscript{2} gases can be readily obtained at no cost by tapping to the exhaust effluent of a combustion system. In fact, this combustion system can burn the bulk of the gaseous fuel generated by the pyrolyzer. A slipstream of the effluent of the very same combustion process can be used to supply the pyrolyzer with a mixture of N\textsubscript{2} and CO\textsubscript{2} gases, upon removal of combustion-generated H\textsubscript{2}O in a condenser. There may be other additional benefits to using CO\textsubscript{2} as the work of Yamada et al.\textsuperscript{22} has shown in the catalysis-aided reforming of the pyrolyzates of PE to CO and H\textsubscript{2} at 950 °C.

A1.2 Experimental approach

A laboratory-scale pyrolytic gasifier system has been designed and constructed to accept granulated plastics, and sequentially liquefy and gasify them. The gaseous pyrolyzates are then mixed with air and burned in a nominally-premixed burner. For demonstration purposes, the burner is also coupled with a miniature steam generator and steam engine setup to produce
electricity (Wilesco D18). The pyrolytic gasifier is shown in Fig. 51. Its major components are a feedstock storing and feeding system and a heating chamber. The feeding system incorporates a reservoir with a hopper where pelletized polymers are stored, an electric motor, and an auger/feeding box. Pellets are gravity-fed from the reservoir through the hopper. The variable-speed electric motor (Leeson Corp. model 985.613F, 8.7 N·m peak torque, 0 – 94 RPM, continuous duty) drives the horizontally-oriented auger which carries the pellets from the feeding box to a vertical purge chamber leading to the furnace. The rotating auger uses a sealed bearing to minimize leakage from the system and, thus, maintain the pressure of the inert carrier gas.

The furnace chamber is defined by a stainless steel tube with a heated volume of nearly 3 liters. This was sufficient to accommodate the expansion of the pyrolyzing polymers, which were fed with a mass feeding rate of 1 g/min, and the flow of the carrier gas, at an additional 1 l/min. The pressure build up during these steady-state steady-flow experiments was only a very small fraction of an atmosphere. The furnace is heated by electrical resistance elements (ATS Series 3110), rated at 1.43 kW. The furnace is connected to a proportional integral derivative (PID) loop temperature controller (ATS Series XT16). This allows for precise and reliable regulation of system temperature at any desired set point. The speed of the electric motor that drives the polymer feeding system is adjusted to obtain the desired mass flow rate of plastic pellets. The direct-drive motor and screw-type auger system provide a linear relationship between feeding rate and motor speed (RPM).

Asymmetrically-perforated disks have been inserted at several vertical locations in the tubular furnace to intercept the falling polymer pellets and facilitate their sequential melting and
gasification. In this manner the particles gasify in the radiation cavity of the furnace, instead of settling at its cooler bottom.

The gas exit tube in the chamber is elevated from the bottom, to prevent its plugging by settling tars, and it is protected by a conical roof to prevent impingement of any falling molten polymer ligaments. Furthermore, the system is fitted with two relief valves, rated at 234 kPa, to avoid over-pressuring.

High-temperature gaskets (THERMA-PUR style 4122 corrugated metal gasket, manufactured by Garlock Sealing Technologies) were used for sealing the flanges. A typical centerline gas temperature distribution in the furnace, as measured by a type-K thermocouple (Omega) is shown in Fig. 52, after correcting for radiation heat transfer. In this case, the controller set-point was set to maintain a constant wall temperature of 950 °C. Temperature measurements were taken at each of the perforated disks in the chamber in order to gauge the uniformity of the heater. The temperature gradient plateaued in the bottom-half of the chamber, where the maximum temperatures prevailed. Superimposed is also a temperature profile calculated by the numerical software *Ansys-Fluent*, as outlined in a following section. The agreement is within 50 °C.
As mentioned before, it has been previously reported\textsuperscript{10, 14, 18, 19} that the yield of gas from pyrolysis of PE increases with temperature; it only accounts for 5.7 wt% at 500 °C, exceeds 90 wt% at a $T_{\text{pyrolysis}} = 800$ °C, and slowly decreases thereafter with increasing temperature. Therefore, a gas temperature of 800 °C was chosen in this work to maximize the yield of gaseous PE pyrolyzates, while minimizing the generation of tars and oils. To account for heat losses throughout the system, the furnace controller set-point was raised to the range of 900-950 °C to ensure reaching 800 °C in the pyrolysis chamber.
A1.2.1 Characteristics of the polyolefin feedstocks

The two polyolefin polymer feedstock materials used in this study were low density polyethylene (LDPE) with a chemical formula of \((\text{C}_2\text{H}_4)_n\), and polypropylene (PP) with a chemical formula of \((\text{C}_3\text{H}_6)_n\). High density polyethylene (HDPE) was not included in this study since it has been previously reported to decompose in a fashion similar to that of LDPE. Commercially available post-consumer plastics, in pelletized form, were obtained from a local supplier and used in these experiments, see Fig. 53. LDPE has a density range of 0.91-0.94 g/cm\(^3\), whereas PP has a density range of 0.86-0.95 g/cm\(^3\).
A1.2.2 Experimental procedure

In each experiment, the pelletized polymers were loaded into the hopper and the feeding system was sealed. The carrier gas is N\textsubscript{2} or CO\textsubscript{2} at a flowrate of 1 lpm. These gases were used to purge the air out of the system and to ensure oxygen-free pyrolysis. Thereafter, the polymer pellets were introduced to the system at a targeted feeding rate. Typical plots of the feeding mass of pellets with time are shown in Fig. 53. To obtain this data, the feeding system was detached from the pyrolysis apparatus and was setup in a bench top style experiment, with a calibrated mass balance (Mettler AE50) positioned to catch and measure the output. The hopper was loaded with plastic pellets and the drive motor was run at constant speed, with manual data readings taken every 5 seconds. The plots shown in Fig. 4 demonstrate fairly linear overall rates of pellets in the broad neighborhood of 1 g/min.

![Image of LDPE and PP calibration results]

**Figure 52: Feeding characteristics of low density polyethylene (LDPE) polypropylene (PP) pellets used in this work. One gram quantities of LDPE (top) and PP (bottom) are depicted on the right.**

In all subsequent experiments the feeding rate of solid pelletized polymers in the furnace was set at 1 g/min, based on experimentally-determined repeatable steady-state operation of the feeder.
This value also matched the capacities of two nominally premixed-flame burners used in this work, a Bunsen burner and a rectangular burner (measuring 2 x 14 cm) supplied with the miniature steam engine (Wilesco D18). In this regard, the capabilities of both burners were tested using bottled ethylene gas (which has been identified as a major pyrolyzate of the polyolefins). Since the ratio of the volume of solid polymer to the volume of gaseous ethylene pyrolyzate is inversely proportional to the ratio of their respective densities (e.g., $\rho_{\text{solid PE}} = 940 \text{ kg/m}^3$ and $\rho_{\text{ethylene}} = 1.178 \text{ kg/m}^3$), the equivalent mass flowrate of ethylene gas to match the mass flowrate of the 1g/min of polymer pellets was determined to be 830 cm$^3$/min. This flowrate of ethylene produced steady flames of appropriate intensity for the operation of the miniature engine.

Additional experiments were also conducted to explore the effect of the carrier gas ($N_2$) on the flammability and stability of the flames. The motivation being, that reduced inert gas flowrates are economically advantageous. Experiments were conducted at the aforementioned ethylene gas flow rate of 0.83 lpm and inert nitrogen flowrates varying by a threefold. These findings of these experiments, in agreement to other pertinent findings elsewhere$^{23}$, showed that the addition of various amounts of nitrogen inert gas did not significantly affect the flammability of the ethylene gas in the nominally-premixed burners used herein$^{38, 24}$.

The pyrolytic gasification chamber contained five perforated steel plates, placed at different axial locations in the furnace tube. The free-falling plastic pellets were intercepted by these plates they heated up and, as they melted, molten mass dripped through the plates, changing state to liquid and then ultimately to gas. Subsequently, the effluent pyrolyzate gases (nominally 0.83 lpm),
mixed with the carrier gas (1 lpm), and then travelled through the exhaust pipe and entered the burner.

A brief series of experiments was conducted to visualize the behavior of molten polymers through the perforated plates. To accomplish this, a quantity of pellets was placed in a stainless steel crucible whose bottom was perforated with several holes, see Fig. 54. A thermocouple was placed in the fixed bed of particles to monitor temperature. The crucible was then heated by an electric tape to temperatures approaching 300 °C. As the temperature of the bed increased the plastic pellets softened, melted (at 250 °C), liquefied and dripped through the holes. As these experiments were conducted under a fume hood at STP conditions, the dripping re-solidified. However, inside the hot environment of the pyrolytic gasifier, it is expected that the drippings will gasify.

Figure 53: Demonstration of melting and dripping of polyolefins through the perforated plates used in the pyrolytic gasifier.24 This experiment was conducted at lower temperatures than those encountered in the pyrolytic gasifier.
A1.3 Numerical approach

A 2D-model has been developed to assess the gas velocity profile and gas temperature distribution in the furnace using ANSYS-Fluent. Based on the velocity profile, a residence time of the pyrolyzates in the heated zone of the furnace was estimated, based on the assumption that the pellets were intercepted by the perforated plates and melted and devolatilized therein. The k-ε model was used for simulating the velocity profile. In this simulation nitrogen was used as the carrier gas at a flowrate of 1 lpm and, in a simplification, the pyrolyzate gases were considered to consist only of one compound: ethylene, which is a major component of polyolefin decomposition. The mass flow rate of ethylene was set at 0.83 lpm. The temperature distribution in the furnace was solved based on the DTRM radiation model, and it was assumed that the source of radiation was the hot wall of the tubular furnace, which was maintained at a temperature of 950 °C (1223 K).

A1.4 Results and discussion

Typical compositions of the pyrolyzates of PE and PP obtained herein are listed in Fig. 55, when nitrogen and carbon dioxide were used as carrier gases. Chemical speciation was conducted with gas chromatography, using a Hewlett Packard 6890 A instrument with flame-ionization and thermal conductivity detectors. In the case of PE pyrolyzed in N₂ at the gas temperature of 800 °C the major pyrolyzates included methane (25.45%), ethane (5.55%), ethylene (31.38%), propylene (7.02%), butadiene (3%), ethylacetylene (1.6%) benzene (4.44%) and hydrogen (21.61%). Ethylene was the most prominent component of the pyrolyzate gas mixture, which is
consistent with the results obtained elsewhere (Goncalves et al.\textsuperscript{7}, Conesa et al.\textsuperscript{10}, Westerhout\textsuperscript{13}, Sawaguchi et al.\textsuperscript{20, 21}, etc.). The H/C ratio in the products of pyrolysis was found to be higher (2.4) than that in the input polymer feedstock (2.0). This indicates that some carbon was removed to the condensed phase. This was indeed the case, as carbon deposits were found on the stainless steel reactor inner walls, upon post-test inspection. After examination, it was concluded that (catalytic) nanocarbon formation occurred therein. An additional experiment was performed with PE at a furnace temperature of 750 °C. The H/C ratio in the PE pyrolyzate output in this case was found to be lower, at 2.06.

In the case of PP the major pyrolyzates included methane (33.37%), ethane (4.77%), ethylene (23.61%), propylene (7.59%), benzene (4.44%) and hydrogen (19.53%). These results differ from results obtained elsewhere\textsuperscript{13, 20, 21}, where propylene was found to have the highest mole fraction. However those studies were conducted at 750 °C, meanwhile the studies herein were conducted at 800 °C. Although primary pyrolysis of polyolefins tends to favor their monomers, it has been reported that higher pyrolysis temperatures\textsuperscript{13} and/or longer residence times\textsuperscript{25} lead to higher yields of methane at the expense of ethylene and propylene. This was the case herein, as illustrated in Fig. 55.
Figure 54: The composition of the effluent of pyrolytic gasification of PE and PP at 800°C and a polymer heating rate of approximately 10 K/sec.

Figure 55 presents data on the pyrolyzate compositions of PE and PP in both N₂ and CO₂ atmospheres. The most notable difference is the higher hydrogen generation in the former environments (N₂), with a concomitant lower hydrocarbon generation.

The role of CO₂ on hydrogen yields in the pyrolysis gases of polyolefins can be put into perspective based on the following overall chemical reaction scheme, which is known as the reverse “water gas shift” reaction.

\[
CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(v)
\]
This reaction is sensitive to temperature, with the tendency to shift towards the products as temperature increases due to Le Chatelier's principle. This is the case herein. In fact, equilibrium calculations using the Stanjan software show that at 800 C this reaction alone can proceed to equimolar concentrations of CO and CO$_2$, if it were given sufficient time. Recent chemical kinetic studies have examined kinetic mechanisms of CO$_2$ addition hydrocarbon mixtures at high temperatures. Liu et al.$^{39}$ studied the chemical effect of CO$_2$ by modeling an ethylene diffusion flame. They added CO$_2$ to the fuel side or to the oxidizer side with a mole fraction of 20%. They illustrated the importance of chemical kinetic effects caused by the CO$_2$ addition, based on the elementary reactions of CO$_2$+H=CO+OH and CO$_2$+CH=HCO+CO. Similar conclusions were also supported by a study of Glarborg and Bentzen$^{40}$ who examined the role of CO$_2$ on the formation of CO. PE and PP pyrolysis experiments performed herein under CO$_2$ atmospheres showed the presence of significant amounts of CO, in contrast to those under N$_2$ atmospheres which showed none.
Nominally-premixed flames generated from continuous feeding of polyethylene and polypropylene in the apparatus, are shown in the photographs of Fig. 56, using the Bunsen burner. In Fig 56(a), a flame of natural gas is shown for comparison purposes. Figs 56(b) and 56(c) show flames of PE and PP, respectively in nitrogen carrier gas. At the estimated nearly-stoichiometric conditions of this work, the natural gas and the PE flames had violet/blue tints, whereas the PP flame was blue with a faint orange surround.

Figure 55: Nominally-premixed flames of (a) natural gas, (b) PE pyrolyzate gases, (c) PP pyrolyzate gases.

As will be shown in Fig. 58, the experimental natural gas flame took place at a nearly-stoichiometric condition ($\phi \approx 0.99$), the polyethylene flame took place at a slightly fuel-lean condition ($\phi \approx 1.1$) and the polypropylene flame was fuel-lean ($\phi \approx 0.90$). Stoichiometric flames have a blue hue due to chemiluminescence of CHO- radicals, fuel-lean flames have a typically violet tint (see the core of the flame) due to chemiluminescence of OH- and CH- radicals, whereas fuel-rich flames have a turquoise green tint due to C$_2$-radicals.$^{37}$
A1.5 Numerical modeling

Predicted temperature profiles in the furnace are shown in Fig. 57, and are in good agreement with the experimental results presented in Fig. 52, which were obtained with a slender bare thermocouple placed along the centerline of the furnace, upon corrections for radiation were made. These results confirm that the temperatures present in the axial and radial directions of the heated section of the furnace are sufficient for maximum pyrolytic gasification (800 °C or 1173 K) yield from the polymer pellets. In Fig. 57, the velocity vectors inside the pyrolysis chamber are also shown. High velocities at the holes of the perforated plates are predicted, and are expected to enhance the polymer devolatilization rates. This ANSYS-Fluent model also predicted a high velocity at the exit of the pyrolysis chamber, which suggests that the chosen carrier gas flowrate is sufficient to force the polymer pyrolyzates through the bottom of the chamber, with no potential for recirculation back up towards the feeding system. The heating rate of the gas was calculated to be in the order of 10 °C/s.
Figure 56: Results of numerical analysis (using ANSYS-Fluent) where gas velocity vectors and contours of static temperature are shown in the pyrolysis chamber.

### A1.6 Combustion effluent analysis

Once the feeding system was developed and fine-tuned to provide a continuous flame, a number of experiments were performed to quantify the affects of different temperatures and carrier gases on the levels of CO and CO$_2$ present in the combustion product gases. The gases were monitored by sampling the effluent of the flames and channeling the slipstream to a *California Analytical Instruments* dual CO-CO$_2$ analyzer, model 200. Given the nature of the burners used, it was not easy to accurately determine the equivalence ratio of their nominally-premixed flames based on the amounts of reactants.

Hence, the equivalence ratio was estimated based on the measured CO and CO$_2$ combustion products. To achieve this, the partial pressures of the combustion products of
pyrolyzate gases were calculated using the chemical equilibrium code STANJAN\textsuperscript{26}. For this calculation, the pyrolyzate gas mixture composition, documented in Fig. 55, was input to the code as reactants (along with the respective carrier gas), and the molar amounts of the major combustion products (O\textsubscript{2}, N\textsubscript{2}, CO, CO\textsubscript{2}, H\textsubscript{2}O, NO, NO\textsubscript{2}) were computed. The calculation was run over several iterations, with the O\textsubscript{2} mole fraction in the reactants altered to produce a range of CO\textsubscript{2}/CO ratios. These ratios are plotted against the experimentally-measured results for comparison purposes in Figure 58. It should be mentioned that data points were obtained at two set-point temperatures of the pyrolytic gasification furnace: 900 and 950 °C. Experiments were run for 20 min and were repeated at least in triplicate; average mole fractions and standard deviations are shown in Figure 58. The scatter in the experimental data is attributed to fluctuations in the feeding rate, as documented in Fig. 53. For comparison purposes, experimental CO\textsubscript{2}/CO data obtained burning natural gas in the same burner, see Fig. 56, are also included in the same figure.

Based on the predictions of the chemical equilibrium code STANJAN, it can be inferred that in most cases combustion took place in the broad neighborhood of stoichiometry, perhaps mildly fuel-lean. Moreover, there was some scatter in the emissions data which may be attributed to some unsteadiness in the pellet feeding and devolatilization as well as to mild fluctuations of the air supply to the Bunsen burner under the operating fume hood. Surprisingly, similar fluctuations in the emissions data were also observed for the case of the natural gas flames, suggesting that the latter mechanism was a significant contributor to this scatter. It may also be observed from these figures that all fuels
resulted in comparable CO$_2$/CO ratios, under the conditions of this work, confirming the
effectiveness of combustion of the gaseous pyrolyzates of post-consumer polyolefins is
akin to that of natural gas.

Figure 57: Experimentally-determined CO2/CO vs. calculated equivalence ratio, $\phi$, at
various implemented

A1.7 On the comparative emissions from indirect and direct combustion of
polyolefins

Indirect combustion of polyolefins, using the scheme implemented herein of first
gasifying the polymers and then homogeneously burning their pyrolyzates with air, is
much less polluting than direct combustion of the same polymers. The former mode of
combustion employs premixed flames, where the fuel-to-air equivalence ratio\(^1\) can be
readily controlled, whereas the latter mode of combustion results in diffusion flames
forming around burning polymer chunks, where the fuel-to-air equivalence ratio cannot
be controlled. Control of the equivalence ratio to an appropriate sub-stoichiometric level
(fuel-lean) can lead to low emissions. Thus such fuel-lean premixed combustion may be
characterized as “clean”. Past results obtained in this laboratory documented that indirect
combustion of polyolefins and other polymers minimized emissions of toxic pollutants.
Gonçalves et al.\(^7\) reported that both the cumulative and the individual component yields
of health-hazardous polycyclic aromatic hydrocarbons (PAH) as well as the particulate
yields (mostly soot and tars) from indirect combustion of pulverized PE in a drop-tube
furnace were more than 10 times smaller than the corresponding yields from direct
combustion of PE in a variety of experimental setups in this laboratory, operated under
diverse of experimental conditions\(^27,28,36\), see Figs 6 and 11 therein. CO yields from the
indirect combustion of PE also appeared to be lower than those from direct combustion of
this polymer at comparable equivalent ratios. Finally, CO\(_2\) yields from indirect
combustion of PE in the case of Gonçalves et al.\(^2\) and in the case herein, as well as in the
case of ethylene combustion\(^36\) were higher than those from direct batch combustion of PE,
reported by Wang et al.\(^34\), which is indicative of more complete combustion.

\(^1\) The fuel-to-air equivalence ratio is defined as \(\phi = \frac{m_{\text{fuel}}/m_{\text{air}}\text{actual}}{m_{\text{fuel}}/m_{\text{air}}\text{stoichiometric}}\)
A1.9 On the replacement of nitrogen background carrier gas with carbon dioxide

Substitution of background N₂ gas with CO₂ was very well tolerated by the flame, producing no discernible differences. As expected, since CO₂ is added to the pyrolytic gasifier input, the amount of CO₂ in the effluent is also higher than in experiments where N₂ was used as the carrier inert gas, see Table 24. Small variations in CO concentrations may be attributed to fluctuations in the polymer pellet feeding rate. The implication of substitution the nitrogen background inert gas with carbon dioxide in the pyrolytic gasifier may prove to be important in the economics of an industrial-scale application. The use of N₂ as a carrier gas requires the procurement, maintenance, and servicing of on-site N₂ gas storage. This is costly, takes up space, and diverts valuable resources to maintaining such a system. CO₂ is a byproduct of combustion, and devising a system to capture the CO₂ as produced from combustion gases to be used as a carrier gas in the system will present significant cost and resource savings, as the CO₂ is produced with no additional cost and diminishing the supply of it is not a factor, as with storing bottled N₂ on site.
Table 24: Average mole fractions of carbon dioxide and carbon monoxide in the combustion effluent of PE, along with computed standard deviations.

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<tr>
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<th>CO₂ carrier gas</th>
<th>N₂ carrier gas</th>
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<tr>
<td>T&lt;sub&gt;set point&lt;/sub&gt;=900 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C O₂%</td>
<td>14.2 ± 1.04</td>
<td>11.1±0.7</td>
</tr>
<tr>
<td>C O%</td>
<td>0.6±0.1</td>
<td>1.5 ±0.5</td>
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</table>

A1.10 Conversion of post-consumer plastics to electricity proof of concept

A technical goal of this project has been to produce a continuous flame with sufficient energy to run the miniature steam engine and produce DC electricity through a generator and to eventually turn on a light bulb, shown in Fig. 59. As mentioned before, a polymer mass feeding rate of 1 g/min generated a flame that was more than sufficient to generate steam and run the miniature steam engine at a high speed. The flame burned with bright bluish colors, see Fig. 59. The steam engine system was able to sustain a boiler pressure of 1 bar and operate consistently at 1800 RPM for duration of an experiment, which was set to 20 minutes. This operational speed was sufficient to use the on board generator to produce a small electric current to illuminate the miniature light bulb. This demonstrated
the concept that waste plastics can be used to produce gaseous fuels with high energy content and, in turn, can reliably generate useful work in the form of electricity, see Fig. 10.

Figure 58: The miniature steam engine in action powered by combustion of pyrolyzates of post-consumer polyethylene in a small burner. The coupled electricity generator powers the light bulb.
A1.11 Conclusions

A laboratory scale system was designed and developed for experimentation. This system is able to pyrolyze pelletized post-consumer (waste) plastics. It was seen that the composition of the pyrolyzates were mostly hydrogen, methane and ethylene. These light hydrocarbons can be easily premixed with air in such a way that the amount of air can be adjusted to reach a desired equivalence ratio.

Power generation was demonstrated with a model steam engine and it was demonstrated that the system was stable and capable of generating electricity for long periods of time (twenty minute tests were conducted herein). Both CO₂ and N₂ were used as background carrier gases for polyolefin pyrolysis and their effects on the pyrolyzate gas compositions were explored. The amounts of light hydrocarbons in the pyrolyzate effluents at the presence of both background gases were similar. The main difference was that a lower amount of hydrogen was detected in the CO₂ environment, and was attributed to water-shift reactions. Future considerations for the system include designing a self-sustaining system in which the electric heater would be replaced by a gas burner, where a fraction of the pyrolyzates would be burned to supply heat to the pyrolytic gasifier.
A1.12 Acknowledgements

The authors would like to thank Massachusetts Clean Energy Center (MassCEC) for financial support through the MassCEC Catalyst Award program and the Garlock Sealing Technologies for the donation of high-temperature gaskets. The authors also want to acknowledge Mr. Christopher Flanagan, Ms. Anna Craver, Ms. Brittne Lynn, Mr. Mason Riley, and Ms. Katherine Dixon for technical assistance in the design and development of the hardware.

A1.13 References

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and poly (ethylene), Symposium (International) on Combustion, 1996; Elsevier: pp 2421-2430.


APPENDIX 2

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A2. A Feasibility Study on Power Generation from Waste Plastics with Partial Pre-Combustion Carbon Capture and Conversion

Abstract

The feasibility of up-cycling waste plastics into concurrent production of carbon nanotubes (CNTs) and of a hydrogen-enriched gaseous hydrocarbon stream was shown to be possible in a continuous steady-state steady-flow process. The feedstock was post-consumer (waste) low-density polyethylene - LDPE, which was pyrolytically gasified at 800° C, in a flow of nitrogen carrier gas. The evolving gaseous hydrocarbon pyrolyzates were first used as carbon growth agents for CNTs in a reactor, a process that lowered their carbon content and increased their hydrogen content. Thereafter, the un-reacted hydrocarbon pyrolyzates and the generated hydrogen were mixed with air and burned. This conversion of solid waste plastics to gaseous fuels allowed thorough mixing with air and, upon ignition, the formation of environmentally-benign fuel-lean premixed flames for subsequent power generation purposes. The CNT generation in the reactor took place by chemical vapor deposition (CVD) on untreated stainless steel mesh substrates, which also served as catalysts. Provisions were made for automatic motion and replenishment of the substrate/catalyst for continuous CNT production. The reactor was specifically designed to have a cold-wall configuration, where only the catalyst substrate was heated to a temperature of 800° C, in an otherwise unheated chamber. This cold-wall reactor has significantly lower energy consumption than conventional hot-wall reactors of similar dimensions and throughput. This work is part of an overall study that aims at illustrating the up-cycling of
common recycled post-consumer plastics simultaneously to gaseous fuels and value-added nanomaterials. Its specific goal was to produce the latter in a newly-designed low energy input reactor.

**Key Words:** Waste plastics, pyrolytic gasification, fuel, combustion, carbon nanotubes, CNTs
A2.1 Introduction

Research Goal: As the global population is increasing exponentially, so also are its energy demands and its generation of solid wastes as well as of air- and water-contaminants. However, finding alternative energy sources to fossil fuels has proven to be challenging and, at the same time, recycling and reusing solid wastes has proven to be limited. This work targets the utilization of post-consumer waste plastics, which are petroleum-based and have the similar energy contents (per unit mass) to those of premium fossil fuels. Given that waste plastics are non-biodegradable and that they generate unsightly litter, their utilization for energy conversion is of both technological and societal importance. The public and commercial interests in their utilization can be further enhanced if their “waste-to-energy” conversion is conducted in an environmentally-friendly manner and if additional value-added products are also co-generated in a cost-effective manner. These are the goals of the research described herein.

The Issue of Waste Plastics: In recent years (Zhuo and Levendis, 2014), the world production of plastics reached 288 million tons, roughly two-thirds of which were contributed jointly by China (~23.9%), European Union (EU-27, 20.4%), USA (16%), and Japan (4.9%). Unfortunately, during the same year, more than 25.2, 32, 28, and 9.3 million tons of plastic wastes were generated in Europe, USA, China and Japan, respectively. A fraction of post-consumer plastics is recycled but most end up in landfills or generate ubiquitous litter. As plastics are non-biodegradable, they generate a long-term
solid waste issue. Even those that are recycled are typically degraded, since they cannot
be easily decontaminated. Direct combustion of post-consumer plastics as fuels in waste
incinerators converts their stored internal energy (heating value) into thermo-electric
power, however, formation of ill-controlled diffusion flames around devolatilizing solid
chunks of polymers generates large amounts of toxic soot and polycyclic aromatic
hydrocarbons (PAHs), as well as other health-hazardous pollutants (Wheatley, Levendis
and Vouros, 1993, Shemwell and Levendis, 2000, Wang, Levendis, Richter, Howard and
avoid this mode of direct combustion and, instead, achieve well-controlled premixed
flames, indirect combustion of solid plastics was implemented herein. A two-step process
was executed, first involving sequential pyrolytic gasification of the solid polymers and
then followed by premixed combustion of the gaseous pyrolyzates with air. Low
emissions of pollutants can therefore be achieved through effective mixing of gaseous
fuel compounds with oxygen(Caponero, Tenório, Levendis and Carlson, 2005, Ergut,
Levendis, Richter, Howard and Carlson, 2007, Gonçalves, Tenório, Levendis and Carlson,
2007, Gonçalves, Tenório, Levendis and Carlson, 2007). Previous work in this laboratory
(Gonçalves, Tenório, Levendis and Carlson, 2007, Gonçalves, Tenório, Levendis and Carlson,
2007) found that the amounts of PAHs and particulates that were emitted from
indirect homogeneous combustion of polyethylene (PE) and of polystyrene (PS)
pyrolyzates were an order of magnitude lower than those emitted from direct combustion of the same polymers, performed under similar furnace operating conditions. Indirect combustion of plastics (i.e., pyrolytic gasification followed by combustion of the pyrolyzate gases) is readily achievable at only a small energy penalty, as Jinno et al. (Jinno, Gupta and Yoshikawa, 2004) reported that the required heat of pyrolysis of common post-consumer plastics (PE, PP, PS) is in the order of 1 MJ/kg. Even after the higher temperatures encountered in the pyrolytic gasification herein (than those of the aforementioned work) are taken into account, the heat of pyrolysis of these plastics is calculated to be in the order of 2 MJ/kg (Soheilian, Davies, Talebi Anaraki, Zhuo and Levendis, 2013). When this value is compared to the heating values (energy contents) of the plastics, which are in range of 40–45 MJ/kg, it becomes apparent that only a small fraction of the heat released during combustion is necessary to be fed back to the pyrolyzer reactor to gasify the plastics. Therefore, the process of indirect combustion of plastics is technologically credible.

Indirect combustion of waste plastics (as well as of other solid fuels) with the intermediate step of gasification (pyrolysis) brings in an additional benefit, that is the possibility of partial capture of carbon from the gaseous stream prior to combustion. In the process developed herein, the carbon is removed from the pyrolyzates and is converted into well-structured carbon nanotubes (CNTs), which are miniscule hollow graphene cylinders with diameters on the order of nanometers (10⁻⁹ m). Their highly organized structure and unique mechanical, thermal, and electrical properties have made
them the subject of extensive research over the past few decades. CNTs are now entering
growth phase of commercialization (De Volder, Tawfick, Baughman and Hart, 2013).

Currently, several methods are used for the synthesis of CNTs, including arc discharge,
laser ablation, controlled flame, and chemical vapor deposition (CVD). CVD is scalable,
and is generally the best suited for mass production. In CVD, a catalyst in floating or
fixed form is exposed to a volatile gaseous carbon precursor, which reacts with the
catalyst to produce a deposit. CNT growth usually takes place on transition metal catalyst
particles distributed on some type of substrate, which is then exposed to a hydrocarbon
gas. The reaction typically takes place at atmospheric pressure in an environment heated
to an elevated temperature, in a range of 600°C to 1200°C. (Kumar and Ando, 2010)

CVD methods, used nowadays in industrial-scale production of CNTs, consume a variety
of costly premium chemical feedstocks, such as ethylene, acetylene, carbon monoxide
(CO), and hydrogen (H₂). Therefore, there is a pressing need for resource-benign and
energy-benign, cost-effective nano-manufacturing processes. In the search for sustainable
alternatives, it would be prudent to explore renewable and/or replenishable low-cost
feedstocks, such as those found in municipal, industrial, and agricultural recycling
streams. (Zhuo, Hall, Richter and Levendis, 2010, Alves, Zhuo, Levendis and Tenório,
2011, Alves, Zhuo, Levendis and Tenorio, 2011, Zhuo, Hall, Levendis and Richter, 2011,
Gong, Yao, Liu, Wen, Chen, Jiang, Mijowska and Tang, 2013, Zhuo and Levendis, 2013,
Gong, Liu, Jiang, Wen, Chen, Mijowska, Wang and Tang, 2013, Wen, Chen, Tian, Gong,
Liu, Rümmeli, Chu, Mijiwska and Tang, 2014, Gong, Liu, Jiang, Feng, Chen, Wang,
Moreover, current methods of carbon nanotube (CNT) production using CVD have long processing times, typically in the order of hours, even though the actual growth of the CNTs occurs in timeframes of the order of minutes. These long processing times are due in part to conventional reactors designs, which are mostly hot-wall batch reactors, meaning that the entire reactor chamber is heated. Heating the large thermal mass of the reactor is inefficient, as it is energy-intensive and time-consuming. Research has shown that it may be only necessary to heat the substrate on which the CNTs are grown and not the entire reactor; these are termed cold-gas (or cold-wall) reactors (Finnie, Li-Pook-Than, Lefebvre and Austing, 2006, Kwok, Reizman, Agnew, Sandhu, Weistroffer, Strano and Seebauer, 2010); in contrast to hot wall reactors (Valles, Perez-Mendoza, Maser and Benito, 2007, Aguiar, Verissimo, Ramos, Moshkalev and Swart, 2009, Kunadian, Andrews, Menguc and Qian, 2009, Yi and Yang, 2010, Koos, Dillon, Nicholls, Bulusheva and Grobert, 2012, Shi, Wang, Wang, Xue, Hou, Cui, Lin, Jin, Cheng, Chen, Yao and Cui, 2012, Zhao, Zhang, Su, Huang, Wei, Kong and Zhang, 2012). Furthermore, research has shown that it is possible to grow CNTs on substrates moving at speeds on the order of 1 mm/s (Villoria, Figueredo, Hart, Steiner III, Slocum and Wardle, 2009).

This work used a pyrolytic gasification apparatus, which was recently designed to continuously process post-consumer (waste) polymers at temperatures in the range of 800–900 °C and generate an effluent stream of light gaseous hydrocarbons and
hydrogen (Zhuo, Alves, Tenorio and Levendis, 2012). Whereas this laboratory-scale apparatus processed recycled plastics in pelletized form, future scaled-up units may be interfaced with polymer feeders that can accept commercially shredded recycled polymers that have different sizes and shapes of variable aspect ratios. This will lower the operating expenses associated with the cost the input feedstock. This apparatus was then interfaced with a newly-designed and constructed apparatus for synthesis of nanoscale carbon in the form of carbon nanotubes, CNTs. To further lower the operating cost of the entire process, this apparatus was purpose-built to be a cold-wall reactor where only the catalytic substrate for the CNT synthesis was heated, not the entire chamber. Upon donating carbon to the CNT formation the gases exiting this synthesis reactor were hydrogen-richer and carbon-leaner. Subsequent to mixing with air, they could be ignited and burned in non-sooty lean-premixed flames, akin those than can be attained in burning natural gas. Heat released from their combustion in boilers or gas turbines may be used for power generation purposes.

**A2.2 Experiment Methods**

**Feedstock Post-Consumer Plastics:** Commercially-available cleaned and pelletized post-consumer low density polyethylene (LDPE), see Figure 60, was obtained from a local waste plastics recycler for the needs of these experiments, as the small laboratory reactor accepted plastics in pelletized form. LDPE has a chemical formula of \((C_2H_4)_n\) and density in the range of 0.91-0.94 g/cm³.
Experimental Setup: The overall process map for the experimental setup is shown in Figure 61. This laboratory-scale setup consists of three components: a pyrolytic gasifier, a cold wall CNT synthesizer reactor, and a nominally-premixed burner. The entire setup was operated in series at steady-state steady polymer flow conditions for the first time in our laboratory. The pyrolytic gasifier system has been designed and constructed to accept a continuous stream of granulated plastics and to liquefy and eventually gasify them (Soheilian, Davies, Talebi Anaraki, Zhuo and Levendis, 2013). The gaseous pyrolyzates then were channeled into the cold wall reactor for CNT synthesis, the effluent from this reactor was subsequently mixed with air and burned in the nominally-premixed burner. For demonstration purposes, the burner can also be coupled with a miniature steam generator and steam engine setup (Wilesco D18) to produce electricity, for details see Ref. (Soheilian, Davies, Talebi Anaraki, Zhuo and Levendis, 2013).

Figure 59: Low density polyethylene (LDPE) pellets from post-consumer recycled plastics.
Figure 60: Overall process map showing the flow of system inputs and outputs

Pyrolytic Gasification Reactor: The pyrolytic gasifier is shown in the left side of Figure 62 and details are given in Ref. (Soheilian, Davies, Talebi Anaraki, Zhuo and Levendis, 2013). Its major components are a feedstock storing and feeding system and a heating chamber. The feeding system incorporates a reservoir (silo) with a hopper, where pelletized polymers are stored, an electric motor, and an auger/feeding box. Pellets are gravity-fed from the reservoir through the hopper. The variable-speed continuous duty electric motor (Leeson Corp. model 985.613F, 8.7 N m peak torque, 0–94 rpm) drives the horizontally-oriented auger, which carries the pellets from the feeding box to a vertical purge chamber, leading to the furnace. The rotating auger uses a sealed bearing to minimize leakage from the system and, thus, to maintain the pressure of the inert carrier gas. The furnace chamber is defined by a stainless-steel tube with a heated volume of nearly 3 L. This was sufficient to accommodate the expansion of the pyrolyzing polymers, which were fed with a mass feeding rate of 1 g/min, and the flow of the carrier inert gas, at an additional 1 L/min. The pressure buildup during these steady-state steady-flow
experiments was only a very small fraction of an atmosphere. The furnace is heated by electrical resistance elements (ATS Series 3110), rated at 1.43 kW. The furnace is connected to a proportional–integral–derivative (PID) loop temperature controller (ATS Series XT16). This allows for precise and reliable regulation of the system temperature at any desired set point. The speed of the electric motor that drives the polymer-feeding system is adjusted to obtain the desired mass flow rate of plastic pellets. The direct-drive motor and screw-type auger system provides a linear relationship between the feeding rate and motor speed. Asymmetrically perforated disks have been inserted at several vertical locations in the tubular furnace to intercept the falling polymer pellets and to facilitate their sequential melting and gasification. In this manner, the particles gasify in the radiation cavity of the furnace, instead of settling at its cooler bottom. The gas exit tube in the chamber is elevated from the bottom, to prevent its plugging by settling tars, and it is protected by a conical roof to prevent impingement of any falling molten polymer ligaments. Furthermore, the system is fitted with two relief valves, each rated at 2 atm, to avoid over-pressurization. High-temperature gaskets (Garlock Sealing Technologies) were used for sealing the flanges. The controller was set to maintain a constant wall temperature of 950 °C.
Figure 61: Experimental setup showing the laboratory-scale pyrolytic gasifier on the left, with the associated pelletized waste plastics storage silo and feeder. The cold-gas CNT synthesis reactor is depicted in the middle. A premixed flame burner is shown on the right.

A schematic of the entire setup is shown in Figure 62, with the outflow of the pyrolytic gasifier connected to the inlet of the cold wall reactor, and the outlet of the reactor connected to a Bunsen burner, which illustrates the utility of the process gas as a fuel for another process. The inputs to the system are the plastic pellets and nitrogen gas, which are fed into the pyrolytic gasifier reactor, and the stainless steel mesh substrate, which is introduced to the cold wall reactor. The stainless steel mesh also serves as the catalyst for CNT synthesis (Zhuo, Hall, Richter and Levendis, 2010, Alves, Zhuo, Levendis and Tenório, 2011, Hall, Zhuo, Levendis and Richter, 2011). The outputs of the cold wall
reactor are CNTs, which are grown on the substrate mesh, and the remaining process gas, a mix of nitrogen, unreacted hydrocarbons, and hydrogen. Nitrogen inert gas is introduced to the pyrolytic gasifier at a rate of 1 L/min., which prevents combustion and drives the pyrolyzate gases out of the system. Before the feeding of granulated plastics commences, the entire system is purged with nitrogen to remove any oxygen that could cause combustion. Once the bulk gas at the pyrolytic gasifier centerline and the gas directly above the heating element in the CNT synthesis reactor are both heated to 800° C, the plastic pellets are fed into the pyrolysis chamber at a rate of about 1 g/min, where they are gasified, resulting in a total gas flow of about 2 L/min, into the cold-wall reactor. After the plastic pellets are introduced, the reel-to-reel substrate feeding system is activated at a linear speed of about 1 mm/s, to allow for CNT growth over a large area of substrate. Once the desired length of substrate has been reacted, the system is powered off and allowed to cool, so that the substrate mesh containing CNTs can be removed and replaced.

**CNT Synthesis Reactor**: The cold wall reactor itself was designed with a focus on low cost, low energy use, and utilizing commercially-available parts where possible. Figure 63 displays a diagram of the reactor design, which features four main components, the substrate heating and feeding subsystems, the gas feeding subsystem, and the overall containment vessel. The substrate heating subsystem uses a 200 W rectangular wire ceramic resistive heating element embedded in insulation, placed directly below the substrate feeding subsystem. The heating element was manufactured by ATS, and has
dimensions of 63.5 mm by 114.3 mm by 17.5 mm. A temperature controller (Thermolyne) with a rheostat was used to achieve and maintain the desired temperature.

Figure 62: Photograph of the Carbon Nanotube Synthesis Cold Wall Reactor

The substrate feeding subsystem features a reel-to-reel cassette which supplies the mesh substrate from a roll placed over the heating element to bring it to the desired reaction temperature, and collects the reacted substrate on another roll. Figure 64 shows the substrate supply system in detail. The system is powered by a 0.42 N-m DC motor with a custom built Arduino based PID speed controller, both of which are mounted outside of
the reactor vessel. A sealed driveshaft transfers power from the motor to the take-up reel. The substrate feeding system was designed for easy loading and unloading of the mesh substrate. The entire cassette slides out from under the gas feeding system, and can be lifted out of the reactor. The reels can then be removed from the slotted channels that they sit in, and readily disassembled to remove the substrate as a roll, with minimal disturbance to the CNTs that grow on the surface of the substrate. A new substrate is then loaded, and the cassette is placed back into the reactor for another run.

Figure 63: Rendering of the Substrate Continuous Feeding System.

In the gas feeding system, the carbon bearing gas is fed over the substrate by a nozzle and a simple conical diffuser, which distributes the gas evenly over the substrate as it moves across the heating element, where CNT growth takes place. The entire system is contained in an airtight thin-walled stainless steel vessel, with external dimensions of 400
mm by 354 by 198 mm. The entire vessel is internally insulated with 25.4 mm of Fiberfrax Duraboard® high temperature rigid alumina-silica fibrous insulation to minimize heat loss. The un-reacted gas is vented through the exhaust port at the rear of the containment vessel for further use, maintaining slightly positive but close to atmospheric pressure in the reactor. In exploratory tests performed herein, the effluent gas from the CNT synthesis reactor could readily ignite and burn in a Bunsen burner, meaning it could be used in further processes, and perhaps to also provide heat for the CNT growth process itself.

A2.3 Results and Discussion

Transient heat up time of the substrate in the cold wall reactor: Tests were performed to assess the transient response of the cold gas reactor, specifically the time it took for the stainless steel substrate catalyst mesh to heat up to operating temperature. As shown in Figure 65, the heat up time to reach 800 °C was approximately 30 min. Thereafter, the substrate feeding motor was activated and supply reel started turning.
Figure 64: Transient heating response of the catalytic mesh substrate in the CNT synthesis cold wall reactor.

Composition of the effluent gases from the Pyrolytic Gasifier: Typical compositions of the pyrolyzates of the post-consumer PE polymer, which exited the pyrolytic gasifier are listed in Table 25. This analysis excludes nitrogen, which was used as the carrier gases.

Chemical speciation was conducted with gas chromatography, using a Hewlett-Packard 6890A instrument with flame ionization and thermal conductivity detectors. In the case of PE pyrolyzed in N2 at the gas temperature of 800 °C, the typical major pyrolyzates included methane (14.75%), ethane (4.58%), ethylene (39.53%), propylene (17.36%), Butene (4.21%), butadiene (5.52%), ethyacetylene (2.17%), benzene (2.74%), and hydrogen (7.93%). Ethylene was the most prominent component of the PE pyrolyzate gas mixture, which is consistent with the results obtained elsewhere (Gonçalves, Tenório,
Table 25: Composition of Polyethylene Pyrolyzate Gases at the exit of the Pyrolytic Gasifier

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mole fractions, excluding N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>7.93%</td>
</tr>
<tr>
<td>Methane</td>
<td>14.75%</td>
</tr>
<tr>
<td>Ethane</td>
<td>4.58%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>39.53%</td>
</tr>
<tr>
<td>Propane</td>
<td>0.54%</td>
</tr>
<tr>
<td>Propylene</td>
<td>17.36%</td>
</tr>
<tr>
<td>Butene</td>
<td>4.21%</td>
</tr>
<tr>
<td>Butadiene</td>
<td>5.52%</td>
</tr>
<tr>
<td>Propyne</td>
<td>0.33%</td>
</tr>
<tr>
<td>Ethylacetylene</td>
<td>2.17%</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.74%</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.33%</td>
</tr>
</tbody>
</table>

This effluent of the pyrolytic gasifier was channeled to the cold wall reactor to prove its effectiveness in generating CNTs. While traversing the cold gas reactor, the pyrolyzate gases served as carbon donors to the CNT growth process. Thus, their composition was altered therein, as carbon was removed from the gaseous phase and was deposited to the condensed phase, with concomitant release of hydrogen via dehydrogenation reactions. Whereas the composition of the pyrolyzates exiting the CNT synthesis reactor was not measured in these feasibility experiments, it was measured in prior work in this laboratory where a hot wall reactor was used under analogous substrate temperature and gas flowrate conditions (Zhuo, Hall, Richter and Levendis, 2010). Therein, the gases that exited that hot wall CNT reactor were overall hydrogen-rich and carbon-lean (H/C = 2.17) by comparison to the gases that exited the pyrolytic gasifier (H/C =2.09) and, even more so, by comparison to the polymer polyethylene feedstock itself (H/C=2). Hence, the overall removal of carbon in that entire process was in the order of 10%. This was in agreement with the deposition of carbon on the substrate to generate CNTs, as observed therein, the yield of which was also in the order of 10% (mass of CNT per mass of polymer feedstock)

Thermal Analysis of the Cold Wall CNT Synthesis Reactor: Due to the nature of the cold wall reactor, where the temperatures of its components differ, comprehensive analysis was performed to ensure that the substrate in the reaction zone is
at the desired operating temperature, which was selected to be 800 °C based on past experiences on identifying effective CNT growth (Harris, See, Liu, Dunens and MacKenzie, 2008, Zhang, Huang, Zhao, Qian, Wang and Wei, 2008, Liu, Yuan, Yang, Elbert and Harris, 2011, Sano, Yamamoto and Tamon, 2012). Another important aspect of the thermal analysis was to determine the performance of the system relative to a traditional hot wall reactor of similar architecture, materials and dimensions. Thermal analysis was conducted both by simple hand calculations and by performing more complex computer simulations.

An important parameter in the design of the CNT synthesis chamber is the magnitude of gas flow over the mesh, to ensure maximum gas and substrate interaction for CNT growth. The exit velocity, $V_2$, of the gas feeding into the chamber via the diffuser is calculated to determine the type of flow and thus the behavior of the gas. The gas from the pyrolyzer exits at a rate of 2L/min and at about atmospheric pressure. Based on the Bernoulli and the Darcy–Weisbach equations and on the dimensions and properties of the system, the exit velocity of the diffuser was calculated to be 1.12 m/s and the associated Reynolds number was $Re=5260$. As Reynolds number greater than 2300 indicates turbulent flow, meaning that the gas will impinge upon the surface of the substrate directly under the funnel, with possible stagnation regions which extend over the surface of the substrate, as shown visually in Figure 66. This implies that the gas will have more time to interact with the substrate to grow CNTs than in a purely laminar flow case.)
Following these calculations, a numerical analysis was performed using computational fluid dynamics (CFD) with the SolidWorks Flow Simulation software. The SolidWorks 3D model of the reactor was simplified for use in the simulation, with small noncritical parts removed, and some complex geometry simplified. The first simulation run (local heating) was of the reactor operating at steady-state steady-flow conditions, with the heating plate maintained at 900° C, and a steady flow of bottled nitrogen (1 atm PSIG) into the inlet at 1 L/min. The second simulation run (global heating) used the same conditions, but applied heating to all inside walls of the reactor, simulating a hot-wall reactor of similar design and dimensions. Results of the simulations depicting the steady-state temperature distributions in the synthesis reactors are illustrated in Figure 67. In both cases the temperature of the substrate mesh was maintained at 800 °C (1073 K).
Figure 66: Steady State CFD Simulation Results – local heating of the mesh substrate/catalyst (top) and global heating of the entire CNT synthesis reactor (bottom).

Predicted power consumptions needed to maintain the gas in the vicinity of the substrate/catalyst mesh at 800° C (1073 K) in the cold wall reactor (local heating) and in the hot wall reactor (global heating) cases are shown in Table 26. It can be seen that the cold-wall reactor was predicted to consume only one fifth the power of the hot-wall reactor to perform this task. In the long run this can result in ample power savings for a scaled-up production system.
Table 26: Numerical Simulation Results on Energy Needed for the CNT Synthesis Reactors

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Energy Consumption (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Wall (Local Heating)</td>
<td>105</td>
</tr>
<tr>
<td>Hot Wall (Global Heating)</td>
<td>510</td>
</tr>
</tbody>
</table>

Growth of CNTs on the stainless steel substrate/catalyst mesh: Upon exposure to PE pyrolyzate gases, which act as carbon growth agents in the synthesis reactor, a sample of stainless steel mesh was examined by both Scanning Electron Microscopy (SEM, Hitachi S 4800 with a working distance of 8 mm and accelerating voltage of 3 kV) and Transmission Electron Microscopy (TEM with accelerating voltage of 80 kV). Results are shown in Figure 68. CNTs with average diameters of 48 nm and average length of 4 µm were detected, covering the surface of the stainless steel meshes.
The CNTs produced in this preliminary study have not been optimized yet. They were produced only to show the feasibility of the newly designed cold wall synthesis reactor, operating in conjunction to the pyrolytic gasification reactor. Generally, nanotube yields depend on several parameters, such as the dimensions of the mesh ribbon, its linear speed and on the flow rate of the pyrolysis gas therein. Past results under batch conditions in a hot-wall reactor showed that CNT yields of 14.5 mg per gram of SS mesh catalyst (Zhuo, Wang, Nowak and Levendis, 2014) can be attained. Whereas, this laboratory scale cold wall reactor only processes 22 g/hr of SS mesh and may produce up to 313 mg/hr, with
further work and optimization, this method can be used to process a lot more catalyst substrate and manufacture CNTs on a larger scale, particularly for use in bulk applications upon removal from the substrate mesh.

Removal of the CNTs from the stainless steel substrates can be easily attained by a brief (a few minutes) sonication in alcohol. Thereafter, past experiments in the laboratory have shown that SS catalyst meshes, can be re-used for growth of CNTs, however, upon each consecutive use the quantity and quality of grown CNTs diminishes. Alternatively, the generated CNTs may find applications where they can remain attached to the stainless steel mesh and used together, perhaps as filters (Zhuo, Wang, Nowak and Levendis, 2014). With further refinement, this cold wall reactor design can provide considerable savings in energy, cost, and time over current CNT production methods.

Combustibility of the gaseous effluent of the CNT reactor chamber: Combustion of the aforsaid partially carbon-depleted / hydrogen-enriched gas under nominally-premixed conditions was readily achieved, as depicted in Figures 62 and 69, using a common laboratory Bunsen burner. Its appearance has been strikingly similar to flames of natural gas burned in the laboratory using the same Bunsen burner forming non-sooty “clean-burning” flames, with a royal blue tint. This is characteristic of conditions in the broad range of stoichiometry. Partial capture of carbon in the CNT synthesis process is expected to reduce the greenhouse causing CO2 emissions. The capability of the pyrolyzate gas from pyrolytic decomposition of post-consumer polyolefins (such as polyethylene and polypropylene) to generate electricity was demonstrated in a previous
study using a miniature burner/boiler/steam/engine. (Soheilian, Davies, Talebi Anaraki, Zhuo and Levendis, 2013)

Figure 68: A flame of polyethylene pyrolyzate gases burning with air; this nominally-premixed flame is anchored on a Bunsen burner.
A2.4 Conclusions

This work demonstrated conversion of municipal waste plastics sequentially into streams of value-added products in the forms of: (a) carbon nanotubes (CNTs) and (b) partially decarbonized gaseous fuel. The fuel is a product of pyrolytic gasification of the polymers in an inert gas, such as nitrogen; it consists of a blend of light hydrocarbons and hydrogen. Burning of the gaseous pyrolyzate fuel constitutes indirect combustion of the polymer and allows for effective premixing with air. Upon ignition of the premixed charge at advantageous equivalence ratios, “clean-burning” flames can be achieved, akin to those consuming natural gas. Combustion of this fuel in a boiler, a gas turbine or a piston-cylinder engine can generate power.

CNTs were successfully grown on a continuously replenished stainless steel mesh substrate utilizing the gaseous pyrolyzates of the waste plastics as carbon donor agents. For this growth a newly-designed cold-wall reactor was used. This reactor needs a much lower power input that conventional hot-wall reactors. The reactor involved a reel-to-reel design for continuously feeding and heating stainless steel mesh that served as both a substrate and catalyst for CNT growth. As this was only a feasibility study, further work is needed to optimize the quality and maximize the yield of the CNT product.

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**A2.6 References**


