



Review

A review – Synthesis of carbon nanotubes from plastic wastes

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ARTICLE INFO

Article history:

Available online 19 April 2012

Keywords:

Multi-walled carbon nanotube synthesis
Virgin and waste plastic
Municipal plastic waste
Waste reduction
Value-added product

ABSTRACT

A large volume of the waste produced across the world is composed of polymers from plastic wastes such as polyethylene (HDPE or LDPE), polypropylene (PP), and polyethylene terephthalate (PET) amongst others. For years, researchers have been looking for various ways to overcome the problems of such large quantities of waste plastics. On the other hand, carbon nanotubes (CNTs) are materials with extraordinary physical and chemical properties which often have energy- and resource-intensive production processes. In recent years, some researchers have suggested the idea of using plastic polymers as the carbonaceous feed of CNT production. The studies undertaking such a feat are rather scattered. This review paper is the first of its kind reporting, compiling and reviewing these various processes. The production of multi-walled carbon nanotubes (MWCNTs) from plastic polymers is seen to be satisfactorily achievable through a variety of different catalytic and thermal methods in autoclaves, quartz tube reactors, muffle furnaces, fluidized beds, amongst others. Still, much work needs to be done regarding the further investigation of the numerous parameters influencing production yields and qualities. For example, differences in results are seen in varying operating conditions, experimental setups, catalysts, and virgin or waste plastics being used as feeds. The area of producing CNTs from plastic wastes is still very open for further research, and seems as a promising route for both waste reduction, and the synthesis of value-added products such as carbon nanotubes.

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1. Introduction

Plastic polymers make up a considerable portion of the volume of waste produced across the world. Although around 5–15% of municipal solid waste is composed of plastics, this waste stream

comprises 20–30% of the volume of MSW. In 2004, about 20 million tons of plastic wastes were produced in Europe [1]. For years, researchers have been looking for various ways to overcome the problems of such large quantities of waste polymers. Currently the use of landfills and incineration are the two most widely spread solutions [2]. However, the increase in costs, environmental concerns, and the decreasing of space for landfills make alternative treatment options desirable [3]. Various alternative routes have

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been proposed in order to process the plastic wastes. Nevertheless, not all these alternatives are used widely, sometimes due to economic viability [4,5].

On the other hand, since their discovery and popularization in the early nineties [6,7] carbon nanotubes (CNTs) have generated widespread interest in most domains of science and engineering; and because of their extraordinary physical and chemical properties, they have been scrutinized for a plethora of functions [8–13]. For instance, their tensile strength is more than 100 times that of stainless steel (≈ 150 GPa) while their density is only about one-sixth (1100–1300 kg/m³); they have a high modulus of approximately 1 TPa, a large aspect (length to diameter) ratio, environmental and chemical stability, thermal conductivities often comparable to that of diamonds (3000 W/m/K), and an electric conductivity comparable with copper [14]. Also important, is the role that CNTs may play as a test bed for fundamental scientific research [15] as well as remarkable properties when utilized as nanocomposites such as CNT sheets known as buckypaper [16].

However, with all this said, the commercial applications of CNTs have still not reached their full potential, and there is still much room for the development of CNT production from waste plastics as a complementary process for large-scale CNT production [17,18]. The current existing methods for CNT production are energy- and resource-intensive, and include (but are not limited to) electric arc discharge method, laser ablation method, catalytic chemical vapor deposition (CVD), flame synthesis, and the solar energy route. Among these methods, CVD seems to currently be the most promising and preferred method for large-scale production [19–21]. Nevertheless, researchers are still looking for more efficient and cost-effective ways for the large-scale production of CNTs. Large-scale production has been defined as the production of 10,000 tons of CNTs per annum [22]. Hence, in recent years there have been efforts regarding possible alternative routes for producing CNTs.

One of the proposed options has been using plastic polymers as the carbonaceous feed. If a feasible process is found which can transform readily available carbon-rich plastic wastes into highly value-added products such as CNTs, considerable profits could be made through simultaneously solving the plastic waste and CNT production shortcomings. However, whilst reviewing the literature, the amount of published studies attempting to synthesize CNTs from plastic wastes were seen to be scattered and limited. As far as the authors are aware, the current paper is the first publication to ever attempt at reviewing the various processes proposed for the synthesis of carbon nanotubes from plastic polymers.

This review is organized based on the reactor types which are used for the synthesis of the nanoproducts.

2. Quartz tube

Some of the first studies attempting to produce CNTs from plastic polymer sources were conducted by a Russian team of researchers in which crooked carbon nanotubes with diameters of 20–60 nm were produced at 800 °C [23,24]. In both studies, granular polyethylene was pyrolyzed in a chamber and the subsequent products were passed over a Ni plate in a quartz tube reactor with a pressure of 4 atm of hydrocarbons and helium (He) gas. The noticeable difference between the two studies is the temperature at which they were performed. In the earlier work, the temperature was chosen to be 420–450 °C, and as a result, crooked carbon nanotubes with diameters of 10–40 nm were synthesized (with a few very thick fibers with diameters of 100 nm). The reaction time was a little less than an hour and the yield of CNT production was approximated at 3×10^{-3} g/cm² per hour. The thermal stability of the products was examined and it was seen that the filamentous

material oxidizes at about 420 °C. This shows the poor quality and deflections of the nanotubes as compared to the oxidation temperature of graphite plates (520 °C) [25]. The existence of impurities in nanotubes is problematic as it has been shown elsewhere that their existence is detrimental to the electronic properties of the CNTs [26]. In the second study [24], it was recognized that the CNTs consisted of nested cones of graphene planes with both the internal and external surfaces possessing open plane edges. The formed layers upon the catalyst plate were several microns thick with the surface showing interwoven carbon filaments 20–60 nm in diameter. After examination of the properties of the CNTs, the researchers concluded that the tube tips protruding from the layer have high electron emission and hence can be utilized as good electron emitters, in photo-emission and electric optic processes, as well as being employed for observing electrochemical processes. Elsewhere, a study concerning field electron emissions showed that the nanotubes synthesized from this method demonstrate a metallic (semi-metallic) type of conductivity [27].

In a following study, nanotubes which were synthesized from polyethylene precursors in the presence of nickel (Ni) as a catalyst, were examined more closely and treated both thermally and chemically by more or less the same team of researchers [28]. The following mechanism steps are speculated to take place in CNT formation: first, carbon dissolves onto the surface of the Ni particles and forms a graphitic monolayer ring. Next, the ring grows in the axial formation while its diameter reduces and the potential of cap formation increases as it sprouts. Finally, the CNT is propagated in the axial direction as a new layer of carbon grows between the first layer and the particle.

Two general nanostructure categories were distinguished. The synthesis of nanotubes has been shown to be influenced by the partial pressure of H₂ gas [29]. The “bamboo” structure was identified and defined when the conical angles along the tubes were 16–35°. These structures were in general a few microns long, had an average outer diameter of 40–50 nm and inner diameter of 9–20 nm. They displayed relatively straight regions with irregular intervals of greatly defected sections. Their layers consisted of open-ended conical graphite layers stacked upon each other. Most of the outer and many of the inner carbon edges are open in these nanostructures. The second nanostructure to be observed is the “fish-bone” which is speculated to be an extreme version of the bamboo type and is defined as when the conical angles along the tube are 75–85°. In these structures, internal caps linked most of the inner layers and the outer layers were also often seen to be linked together. When reaction temperatures were low, only “fish-bone” filaments were found, whereas, when reaction temperatures increased more “bamboos” emerged.

After the products were produced, various heat treatments at high temperatures were conducted. The fish-bone nanostructures have minimal changes, but the bamboo style nanotubes are altered. Treatment temperatures of 1200 °C, 2000 °C, and 2800 °C were tested, and more edges were seen to be linked by loops until all neighboring edges became completely linked at 2800 °C.

During the chemical treatments it was shown that both CNT types withstood bromination without detrimental effects on their structures. However, when a treatment of concentrated HNO₃ was conducted, the CNTs were completely destroyed. Finally, the treatment of the nanotubes with molten V₂O₅ resulted in no penetration into the channels or between the layers. In addition, it induced extensive linking of neighboring carbon layers.

Low density polyethylene (LDPE) has also been a potential carbonaceous source for CNT production. In a study [30] thin-walled nanotubes were synthesized by using LDPE as a precursor, under nitrogen flow, in the presence of a uniformly distributed iron hydroxide catalyst (weight ratio of 1 part catalyst to 20 parts dry LDPE). O-xylene was used to mix the components suitably as

o-xylene could then be evaporated at room temperature. The heating rate was 150 °C/h and there were 2 h holding periods at 250 °C, 400 °C, 600 °C, and 750 °C. The produced samples were in turn treated, washed, and dried overnight. The purification process did not harm the CNTs. When observing the products it was seen that there is a huge difference between what is produced at 600 °C and 750 °C. The former being covered with undesirable disordered amorphous carbon, and the latter containing agglomerates of hollow CNTs. The nanotubes had an average diameter of 20 nm and an average length of 300 nm. The mean thickness of their walls which were formed from disordered graphene sheets was approximately 3 nm. Also, a quantity of carbon shells which enclosed some catalyst particles were seen in the inner cavities. Reasons as to why these two types of nanostructures are seen were provided.

A year later and in a similar study, the same investigators [31] attempted to describe the mechanisms involved in the synthesis of CNTs from PE and polyvinyl alcohol in the presence of iron hydroxide catalyst. The thermal decomposition of the mixture had been previously investigated [32]. The use of polyvinyl alcohol was singled out for an analogous study a year later [95]. The process used to form the CNTs, as well as most of the work, is very similar to the group's previous study [30]. The researchers speculated that the Iron metal produced from the iron hydroxide collects carbon on its surface in the form of Fe–C intermediates. The accumulation of the intermediates is succeeded by their liquidation and movement to form cockle-shelled filaments in the bulk of the amorphous carbon matrix. The formed filament aids the transport of catalysts throughout the matrix surface. Next, MWCNTs are formed in the pore voids of the matrix. Finally, the nanotubes having catalysts at their ends break away from the cockle-shells.

As a continuation of their previous work, the effects of catalyst size on the dimensions of the produced CNT from PE were also studied [33]. The method of CNT production was similar to [23]. CNTs were grown at both 700 and 800 °C in the presence of a Ni catalyst with a known size distribution. The experiments show that the case for catalyst size dependence is very different at the two temperatures. Particle mobility, sintering and redispersion complicate the matter to a great extent. Hence, if special care is not taken to suppress the aforementioned complications, using particular catalyst sizes as a scheme for controllable CNT growth must be approached with caution. Nevertheless, immobile catalysts used at the lower temperature (700 °C) at which nanotube growth occurs via solid tip catalyst particles, lead to a distinguishable similarity between nanotube diameter and particle size distribution. As temperatures rise, catalyst particles liquefy, are saturated with carbon, and nanotubes grow via extrusion. Interestingly, at 800 °C, a Gaussian distribution of CNT diameters (average 40 nm) is seen irrespective of the catalyst particle size distribution. For PE feeds in the presence of Ni catalysts, the sensitivity of nanoproductions on the process temperature has also been shown by Blank et al. [34].

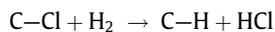
Elsewhere, and more recently, the vacuum pyrolysis of polypropylene with iron nanoparticles (with an average particle size of 17 nm) was used to synthesize carbon nanotubes [35]. The morphology seemed to be governed by the competitive processes between catalyst coalescence and CNT growth. 1.8 g of PP was mixed with 0.02 g of catalyst and 20 ml of p-xylene in order to prepare the precursor. Film-typed specimen (about 600 nm in size) were produced from the precursors by spin-coating them onto silicon wafers. These specimens were then preheated to remove solvents and subsequently pyrolyzed in the furnace with pressures below 6.7×10^{-5} mbar. When compared to other studies, the amount of catalyst used in this method is minimal. Through correspondence with the authors, they speculated that such small amounts of catalysts were enough, maybe due to their small size. The formation of MWCNTs was seen up to 900 °C prior to the coalescence of iron particles larger than 100 nm. At 700 °C, tubes

with wavy carbon layers to the tube axes and diameters of 16.5–40 nm (with wall thickness of 3.8–14 nm) were synthesized with morphologies similar to CVD-grown MWCNTs [36]. In the same study, and as a comparison, polystyrene (PS) was also used as the carbonaceous source. The formed CNTs (with diameters of 7.5–25 nm) had thick walls when compared to those derived from PP.

Chung and Jou [35] go onto state a possible reason for the difference in the produced CNTs by using various references: "Olefins are the main products from thermocatalytic decomposition of PE and PP, whereas aromatic hydrocarbons are produced from decomposing PVA and PS in the presence of catalyst. Therefore, the reactions between the olefins and the catalysts may cause the growth of long CNTs during the pyrolysis of PE and PP. On the other hand, the aromatic hydrocarbons generated from decomposing polymers might facilitate the wall thickening by the secondary pyrolytic deposition on the surface of the CNTs." In the end, this method is not proposed for mass CNT production of high purity, but such a process could be used for the alteration of char residues of degraded polymers [35].

Very recently, a study has investigated the possibility of synthesizing vertically aligned CNTs with a two stage plastic pyrolysis and CVD method [37]. In the procedure, 0.1 g of ferrocene was fixed in a section of the quartz reactor and sublimated. Then, the 2.0 g of PP already fixed in a different position was pyrolyzed at 450 °C. Finally temperatures are elevated to 800 °C in the CVD zone where CNT array growth occurs. Ar and H₂ gas (50:3 vol.%) were present throughout the reactor. The produced products were scraped off with blades for assessment. Although PP was generally used in the study, the researchers went onto use PE and PVC as well, to show that the process is not limited to a particular type of plastic. The initial synthesized nanotubes consisted of woven structures, but as the array grew and large space resistance was met in the horizontal directions, the CNTs grew vertically while forming ordered structures. Applications of carbon nanotube arrays are often very much sensitive to the diameter of the CNTs. Thus the researchers proceeded to consider the effects of the catalyst feeding rate and size as well as the process temperature on the produced CNT array. The increase of catalyst feeding rate decreased the mean diameter of the CNT from 36.0 nm to 22.6 nm. Much more catalysts were used in this experimental setup than seen in some other works. In addition, the size of the catalyst strongly affected the diameter distribution of the produced CNT arrays. When the temperature was increased to 850 °C rather than 800 °C, the products showed lower defect density, the iron catalyst particles became larger in size and, CNTs with larger diameters were produced in array form.

Comparatively, the products produced from PE showed good morphology and had a clean surface. However, the chlorine in PVC eventually partly poisoned the catalyst and thus, the CNT arrays derived from PVC were entangled more densely. Fortunately, no traces of chlorine were detected in the CNT array. This is due to the fact that at those temperatures and in the presence of Ar and H₂, Cl is substituted via the reaction:



In this study the relationship between the time of growth and the length of the produced CNT arrays was observed. The researchers concluded that longer growth times led to lengthier CNTs. For PP, the average growth rate of 12 μm/min was estimated for CNT arrays with a length of 500 μm and a growth time of 40 min. It should be noted that although these figures are acceptable, these growth rates are still lower than when other hydrocarbons such as cyclohexane and xylene are used as sources of carbon [38,39].

The advantage of this innovative process compared to previously mentioned studies using plastic feed is that here, the obtained products are vertically aligned.

Elsewhere, Zhuo et al. [40] presented an exothermic and scalable method for producing CNTs from separate plastic wastes, namely PE, PP, and PS. First, the solid polymers were pyrolyzed at temperatures of 700–900 °C in the presence of flowing N₂ gas as an inert carrier. Then, the resulting effluents were combusted with air (PS effluents were not mixed with air as they did not need additional oxygen). Finally, meshes of stainless steel type 304 were used to synthesize the nanotubes via CVD. The range of effluents which resulted from the first pyrolysis step included both light aliphatics and aromatics. The combustion step introduced CO and CO₂ which have also been known as possible carbonaceous sources for CNT growth. The presence of H₂ and H₂O are also favorable, as they have been proven to keep catalysts active [41]. Since the pyrolysis of plastics is an exothermic process, if the produced energy is correctly harnessed and utilized, it is more than enough to provide the requirements of the subsequent steps of CNT production.

The products were smooth with lengths of 3–6 μm. If the combustion step is bypassed, there is not a major difference between the morphologies of the products. Various differences are noticed when comparing the products of various carbonaceous sources and production patterns. However, due to the limited length of the study, findings should be viewed cautiously.

The details of the previous study, the laboratory apparatus, and the quartz tube process were explained thoroughly earlier [42]. It is notable that the combustion step takes place as the pyrolysis effluents enter a venturi where they are mixed with air or oxygen-rich air. Auto-ignition occurs, keeping in mind that the ratio was kept to be considerably fuel-rich in order to keep much of the carbonaceous precursors intact. Some soot was created in an order to prevent it from coming into contact with the catalyst and cause deactivation, a high-temperature silicon carbide (SiC) honeycomb barrier filter was used. Although Tribolet and Kiwi-Minsker [43] have shown that it is not always easy to remove the CNT from the substrate, here, in order to remove the products from the mesh surface ethanol was conveniently used. When post-consumer HDPE was used as the feed, and operating temperatures were fixed at $T_{\text{pyrolysis}} = 800$ °C, $T_{\text{synthesis}} = 750$ °C, with 50% O₂ mole fraction at the venturi, MWCNTs with diameters of 15–84 nm and lengths of 1–5 μm were produced on all sides of the woven wire stainless steel mesh.

Some defects can be seen on the produced tubes. Generally, defects in CNTs reduce the mechanical strength, lessen the electric conductivity, cause energy concentration points and result in premature failure. However, increasing operation temperatures and residence times have been known to increase the degree of graphitization leading to the reduction of defects [44].

TGA analysis of the products shows considerable weight loss emerging after 450 °C and finishing by 600 °C. The BET surface area of the synthesized products were rather low at 76.3 ± 0.9 m²/g. The researchers suggested that such values might be appealing for Li storage in Li-ion batteries, where high surface areas are unwanted in order to avoid irreversible adsorption in those applications. The researchers went on to carry out parametric studies on various operating parameters. Very interestingly, a cursory examination of the morphologies of the produced CNTs showed no major difference between products from milk jugs (HDPE) and news paper wraps (LDPE). Also, no major difference was seen between pre- or post-consumer PE feedstock. Nevertheless, more investigations and characterization work are needed in this regard.

CNTs are produced whether the combustion step exists or not. However, with the combustion step in place, as the oxygen mole fraction in the flame increases, the diameters of the tubes decrease,

they become smoother, and longer. Thus there might be a correlation between the existence of CO and this quality upgrade.

In another parametric analysis step, various coatings of the stainless steel were considered. When the stainless steel was covered with a 4 nm cobalt coating, distinct features such as straight, tortuous and coiled shaped nanotubes with rather steady thicknesses but a highly variant diameter distribution (20–100 nm) were seen. When the steel was coated with 4 nm of Ni, no irregular and coiled structures were seen and a more or less uniform diameter distribution was present. It was observed that the nanoparticles attached to the ends of CNTs consisted of not only nickel, but of iron, chromium, and manganese, which are usual components of the stainless-steel as well. Still, much more research is needed to accurately understand the effects of various parameters and operating conditions.

Thermal annealing in a quartz tube furnace has also been investigated. Sarangi et al. [45] performed two sets of experiments with diamond-like carbon (DLC) and polyethylene as hydrogen-rich carbon sources for the synthesis of nanomaterials via vacuum annealing in a quartz tube furnace. It should be noted that throughout their work, “polyethylene” is abbreviated as “PET”. It was at first unclear whether the researchers had deviated from the accepted abbreviation of PE for polyethylene mistakenly using the abbreviation associated with polyethylene terephthalate; or in fact, polyethylene terephthalate was used as the carbonaceous source. Through correspondence with the authors, it was clarified that in fact the abbreviation was used incorrectly, and that polyethylene had been used. The PE was commercially bought and mixed with a catalyst (half Ni half PdCl₂) prior to the process. The annealing was performed in the presence of argon (Ar) gas. The inner furnace quartz tube was first vacuumed to $\sim 10^{-5}$ Torr. The samples were maintained inside the tube reactor for 3 h whence temperatures rose to about 1000 °C. Again, due to poor penmanship, there is confusion as to whether the operation was done at 1000 °C or 1200 °C. Results showed that the use of PE as the feed led to the formation of peculiar and totally amorphous nanostructures. The structures had diameters between 40–80 nm which decreased throughout the short lengths of the nanotubes, much shorter than those produced from the DLC. The produced nanostructures were horn-like, had a metallic particle at their base, and were almost always capped by a smaller metal particle. An explanation based on the previous work of Oberlin et al. [46] was provided for the morphology. The variation of catalyst amounts had a strong effect on the nanostructure formation.

Nonetheless, this method of CNT production requires high temperatures for a rather lengthy period of time and thus this research does not appear promising compared to some other alternatives for producing CNTs from plastic polymers. A summary of the key studies in which quartz tube reactors have been used can be seen in Table 1.

3. Autoclave

Kong and Zhang [47] were able to produce high yields of CNTs with diameters from 20 to 60 nm from PE in an autoclave at 700 °C. In the process, they were also able to produce 5% helical CNTs. In general, carbon nanotubes are seen in various shapes other than straight, such as helical, curved, and planar-spiral [48]. Helical CNTs have been verified to have distinctive electrical, magnetic and mechanical properties and are of particular interest in the nanoelectromechanical domains [49]. Here, regarding the production of helical CNTs, the researchers speculated that this might be due to the catalytic pyrolysis of acetylene which is itself produced as an intermediary byproduct of the PE and MA-PP degradation.

Table 1
Summary of key studies utilizing quartz tube reactors.

Reference	Polymer	Reactor type	Temperature (°C)	Pressure	Reaction time	Catalyst	Length of CNT	Diameter (nm)	Product description
[23,24]	PE	Chamber + quartz tube	420–800	4 atm	50–60 min	Ni plate in the presence of He		10–60 nm	As temperatures rise, diameters increase
[28]	PE	Chamber + quartz tube	500–800	4–5 atm	15–20 min	Ni plate in the presence of He	Few μm	40–50 (bamboo), 9–70 (fish-bone)	
[30]	LDPE	Quartz tube	750		Several hours	Iron hydroxide (1:20 wt.%) uniformly distributed in the bulk of the polymer in the presence of Nitrogen	300 nm	20	600 °C is inadequate and leads to amorphous carbon
[33]	PE	Chamber + quartz tube	700 800	Presumed 4 atm	Presumed 50–60 min	Ni in the presence of He		10–100 dependent on catalyst particle size Gaussian distribution with average diameter 40 independent of catalyst size	
[35]	PP PS	quartz tube	700–900 700	Under 6.7×10^{-5} mbar	1 h	Iron nanoparticles (1:90 wt.%) 10–50 nm		16.5–40 7.5–25 with thick walls	Higher temperatures produce shorter CNTs
[37]	PP PE PVC PP	Quartz tube	Pyrolysis at 450, synthesis at 800 Synthesis at 850		30 min	Ferrocene (0.1–0.8 g/min) in the presence of Ar and H ₂ (50:3 vol.%) Ferrocene (0.2 g/min)	Lengths up to 500 μm obtained with rate of 12 $\mu\text{m}/\text{min}$	Mean 22–36 Mean 34.4	Clean with good morphology More entangled, worse quality, partly poisoned catalyst
[42]	HDPE	Quartz tube + oxidation venturi + quartz tube	Pyrolysis at 800, synthesis at 750		Up to 1 min	304 Stainless steel with cobalt, nickel, or no coating	1–5 μm	15–84 nm with mean of 43.6. As oxygen increases in the flame, diameters decrease, and CNTs become smoother and longer	Cobalt coating leads to irregular and coiled structures with variant diameter distribution. Ni or no coating, lead to no irregularity

In the procedure, 2.0 g of PE, 0.5 g MA-PP and 0.5 g of ferrocene were maintained at 700 °C in a sealed autoclave for 12 h and subsequently reduced to room temperature naturally. Many dark residues and some gases were produced. The residues were collected, washed thoroughly, and dried under vacuum conditions for 4 h. The effect of the pyrolysis temperature was examined and it was seen that the reaction initiated at 400 °C with mainly amorphous carbon products. However, as temperatures rose, so did CNT yields. At 700 °C the product consisted of 80% CNTs. It was also observed that in the absence of MA-PP, the Fe would agglomerate at the bottom of the autoclave and CNT production would be greatly reduced. So in fact, MA-PP was acting as a compatibilizer for the improvement of Fe dispersion in the substrate.

Just a few months after the previous publication, Zhang et al. [50] again published a similar study. The only main differences

between their two studies were that this time, polypropylene was used as a reagent instead of polyethylene in addition to Ni being used instead of ferrocene. The average outer diameters of the synthesized CNTs of 160 nm were much larger than the previous experiment; the thickness of the walls averaged at 45 nm. However, the yield still remained as high as 80% (at 800 °C operating conditions). When no catalyst was used, carbon spheres were the only products to be produced. It is also speculated that MA-PP might slow down the velocity of the carbon atom distribution on the catalyst surface, and in turn promote graphite layers forming CNTs.

Zhang et al. [57], also produced jumbled CNTs in the form of microspheres with diameters of 5.5–7.5 μm by pyrolysis of PP, maleated PP, and ferrocene [Fe(C₅H₅)₂] in an autoclave. The reactor containing the unmixed composite of PP/MAPP/ferrocene (2/0.5/

Table 2
Summary of key studies utilizing autoclave reactors.

Reference	Polymer	Reactor type	Temperature (°C)	Pressure	Reaction time	Catalyst	Length of CNT	Diameter (nm)	Product description
[47,50,57]	PP	Autoclave	800		12 h	MA-PP and Ni MA-PP and ferrocene		Average 160 with thick 45 nm walls	Jumbled CNTs in the form of microspheres, with relatively rough walls
			600					35–55	
			700					Tens of microns	
	PE						20–60	With lower temperatures, CNT yields decreased	
[51]	HDPE, LDPE, PS	Closed autoclave	700	Builds up to 1200 psi	2 h	20 wt.% CoAc	1 μm	Average 80	CNT lengths increased with reaction time

0.5 wt.%) was sealed and maintained at 600 and 700 °C for 12 h. The dark products were then cooled to room temperature naturally, collected, treated, washed, and vacuum dried for 6 h.

The CNTs composing the microspheres at 600 °C have rougher walls and outer diameters in the range of 35–55 nm. However, at 700 °C, large amounts of less-jumbled and smooth nanotubes with outer diameters of 40–70 nm, inner diameters of 7–30 nm, and lengths up to tens of micrometers are attained. Also, better crystallinity of products with fewer defects was seen for products synthesized at 700 °C. The BET surface areas for the products at 600 °C and 700 °C are 140.6 and 74.5 m²/g. An advantage of this process compared to some other sphere-producing processes is that here, premixing is not required.

Pol and Thiyagarajan [51] also showed the possibility of creating MWCNTs from the thermal decomposition of HDPE, LDPE or PS in an autoclave at 700 °C in the presence of cobalt acetate catalyst. The reactants were placed inside the sealed reactor in order to ensure that the resulting decomposition gases remain in proximity of the catalyst and facilitate nanotube production. As temperatures rise in the autoclave, the pressure increases. Before 680 °C, the pressure is no more than 50 psi. However, when the temperature reaches 700 °C, the pressure swells to 1000 psi and continues to grow to 1200 psi. Conversion of the plastics into carbon nanotubes required a minimum of 20 wt.% CoAc catalyst. No catalysts, as well as low amounts of catalysts, result in carbon sphere production [52,53]. The average diameter of the MWCNTs was 80 nm. With the increase of the residence time, so did the length of the tubes. After 2 h, the nanotubes grew to lengths of more than a micron in protruding bunches – each bunch comprised of hundreds of MWCNTs. As far as the morphology is concerned, it was speculated that initially, a graphene cap formed on the catalyst. Then, subsequent caps formed underneath the prior, forcing older caps to rise higher in the form of a tubular structure. The cobalt nanoparticles are trapped. If MWCNTs are wanted without metals, acidic treatment is needed to dissolve the catalyst particles. The magnetic properties, electrical conductivity, and absorption characteristics of the products were examined. Pol and Thackeray [54] went onto produce high purity nanomaterials from various polyethylene products with their autogenic method. The synthesized materials were used in lithium half cells as electrodes with favorable results. Comparatively, the results were better than the reversible capacity of MWCNTs produced by a traditional arc-discharge method (125 mAh/g) but slightly lower than MWCNTs from the catalytic decomposition of ferrocene and xylene (250 mAh/g) [55,56]. A summary of various studies in which autoclave reactors have been used can be seen in Table 2.

4. Crucible

In a simple reactor crucible Song et al. [58] used two kinds of zeolites (HZMS-5 or H-Beta) as synergistic additives to encourage

the synthesis of multi-walled carbon nanotubes from polypropylene (PP) via combustion in the presence of Ni₂O₃. The PP was first mixed with Ni₂O₃ (*d* < 50 nm) and then with the chosen zeolite in a Brabender mixer at 100 rpm and 190 °C for 10 min. In order to produce the as-prepared MWCNTs, about 5 g of the resulting mixture was burned at 700 °C in an open crucible. The residues were collected and treated (purified) with HF and HNO₃ to eliminate remaining zeolites, amorphous carbons, and most of the Ni(0). Subsequently, the morphologies and micro structures of the synthesized products were examined with SEM and TEM. It was found that the products of the H-Beta zeolite (PP/H-Beta/Ni₂O₃: 90/5/5) were more favorable and contained an abundance of hair-like fibers which had a rather uniform distribution of diameters. In addition, no other morphologies of carbonaceous species were created, the walls of pristine CNTs mainly consisted of graphite fringes, and there was little sign of attached amorphous carbon on the outer surface of the tubules. Nevertheless, the products were not perfect and numerous defects still appeared in the alignment of the graphite layers, which resulted in the distortion and disconnection of many coaxial tubes. The highest obtained yield was 52% (percent of purified charred residue to plastic polymer input).

The second zeolite to be used was H-ZSM-5. Again, the results showed the formation of hair-like fibers. However, the diameters were variant and bigger than the previous products. Additionally, the procedure resulted in considerable amounts of amorphous carbon and carbonaceous particles. Overall, it was concluded that under similar operating conditions, the synthesis of MWCNTs from PP/H-ZSM-5/Ni₂O₃ systems resulted in much lower yields and qualities than from PP/H-Beta/Ni₂O₃. The reason for the better performance of H-Beta can be attributed to the fact that H-Beta is a large pored, strong acidic molecular sieve which fragments under high temperatures exposing more acid sites which facilitate MWCNT formation. The TG analysis of the products showed that the decomposition process was effectively seen after 500 °C with a maximum value at 590 °C, indicating good stability.

The above mentioned study was in fact an extension of a previous one. In a study published years earlier, Tang et al. experimented with a similar set up [59]. In that study, polypropylene was mixed with an organic-modified clay, a nickel catalyst, and maleated polypropylene in the same Brabender mixer at 100 rpm at 190 °C for 10 min. Then the mixture was heated in a crucible at 600 °C. The remaining char residues were cooled and purified as previously explained. The morphologies of the purified products were in turn examined and large quantities of hollow tube-like structures with diameters of 20–40 nm were found. It was speculated that the presence of clay in the combustion would assist MWCNT formation. The researchers mention that the effects of various process conditions should be examined and that the process could possibly be used for other polymer systems. These claims were left to be answered in their future work.

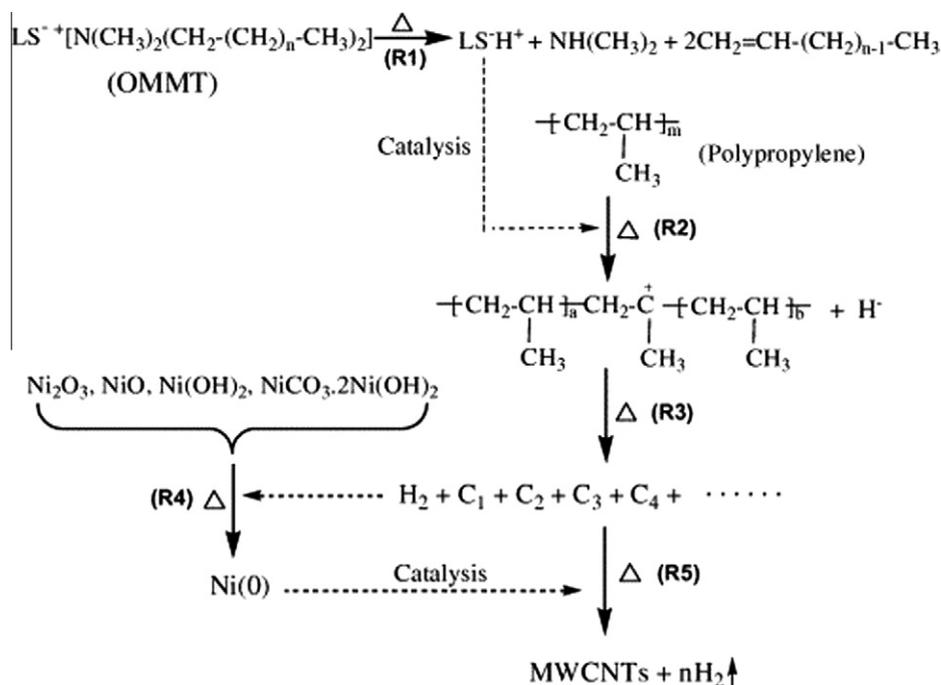


Fig. 1. Possible reaction mechanism proposed by [60] for the synthesis of MWCNTs from PP in the presence of catalysts (LS = MMT).

Table 3

Summary of key studies utilizing crucible reactors.

Reference	Polymer	Reactor type	Temperature (°C)	Reaction time	Catalyst	Length of CNT	Diameter (nm)	Product description
[58–60]	PP	Crucible	700	Short burning	Ni ₂ O ₃ (5 wt.%) with HZMS-5 (5%) or H-Beta (5%)		H-Beta lead to uniform diameter distribution but H-ZSM-5 resulted in variant larger diameters	H-Beta resulted in mainly CNTs while H-ZSM-5 lead to some other amorphous products as well
			600–830		OMMT, Ni, and maleated PP	Wide range, mainly 20–60		Higher temperatures and more OMMT resulted in higher yields

More or less the same group of researchers participated in another study [60] in which multi-walled carbon nanotubes (MWCNTs) were successfully produced through the combustion of polypropylene (PP) using nickel compounds such as Ni₂O₃, NiO, Ni(OH)₂ and NiCO₃·2Ni(OH)₂ as catalysts. These catalysts were employed in a crucible in the presence of organic-modified montmorillonite (OMMT) clay. The researchers observed the morphologies and stated that the yield of MWCNTs was influenced by PP, OMMT, and nickel compound mixing compositions as well as the

combustion temperature. It is believed that due to the Hoffman reaction of alkyl ammonium, proton acidic sites on the degraded OMMT layers altered the degradation reaction mechanism of PP from thermal to catalytic. This in turn facilitated the nickel catalyst to synthesize higher yields of MWCNTs. So the existence of OMMT played a pivotal role in the process. In all samples it was seen that if 10 wt.% OMMT was added to the mixture which did not contain any of the clay to begin with, the MWCNT yield would increase at least by 39%. Sometimes only a 5 wt.% addition of clay would have such drastic effects. It should be noted that the actual active site of MWCNT growth is the Ni(0); which was formed as the consequence of the reduction of the nickel compounds with the aid of hydrocarbon gases resulting from PP degradation as well as hydrogen. Fig. 1 shows the possible reaction mechanisms proposed.

Overall, the particular difference of this study with the previous work [59] was that in this study, it was shown that OMMT could importantly enhance the otherwise low yields of MWCNT synthesis. As confirmed by the literature, the use of OMMT in the PP/PPMA mixture also added to the increased production of liquid products [61]. Elsewhere, it has also been shown that organophilic montmorillonite (OMT) clay could be used alongside Fe catalyst for synthesizing good quality carbon nanosheets (2–8 nm thick) from polystyrene. The existence of OMT helped to increase the yield because it assisted to clutch the pyrolytic aromatic hydrocarbons

Table 4

The effect of various metals on CNT production (the weight ratio of PP/Nmm-cat is equal to 97/3) [63].

Ni(NO ₃) ₂ /(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O/Mg(NO ₃) ₂ mole ratio	Yield of CNTs (wt.%)
5/0/0	5
5/0.2/0	8
5/0.15/0	16
5/0.05/0	18
5/0.1/0	34
5/0.1/0.25	41
5/0.1/1.5	48
5/0.1/0.5	49
5/0.1/1.25	51
5/0.1/1.0	58

produced from PS degradation from escaping from the quartz tube reactor at 900 °C [62].

R1–R5 represent the various steps of the synthesis as follows [60]:

R1: Thermal decomposition of the modifier leads to the formation of proton acidic sites on the degraded OMMT layers (LS–H+).

R2: Cationic active sites are formed as the proton acidic sites attack the PP molecular chains.

R3: PP is degraded catalytically.

R4: Some degradation products of PP reduce some nickel compounds to Ni(0) in situ.

R5: Degradation products are catalyzed to form MWCNTs, possibly via a dissociation–diffusion–precipitation process.

Since the temperature needed to degrade polymers is lower than that needed for synthesizing polymers, most degradation products leave the system as gas before CNTs can be produced resulting in low yields. Therefore catalysts such as Ni (having the highest activity from among the Fe groups) are applied. However the lifetime of the catalyst is short because of the amorphous carbon which coats its surface. Hence H₂ is used in order to increase catalyst life by removing the amorphous carbon [63]. When no clay is present, trace amounts of halogenated compounds alongside Ni₂O₃ lead to a synergistic catalysis and promote the formation of the residual char through the dehydrogenation–aromatization of PP degradation products. Flame retardancy is improved and longer fiber-like structures are produced [64]. A summary of various studies in which crucible reactors have been used can be seen in Table 3.

5. Muffle furnace

In their most recent study, Song and Ji [63] have demonstrated a considerable improvement to their previous usage of Ni for CNT production from PP by adding Mo and Mg to the catalyst. These catalysts were combusted and prepared by the method of Li et al. [65]. Then the catalyst was mixed with the substrate to form a composite in a Brabender mixer. The composite was then placed in a crucible and heated in a muffle furnace at 850 °C for 10 min. After cooling to room temperature the produced black powder was observed without any further treatment or purification. Table 4 shows the various yields of CNTs compared to the catalyst composition. The yield is calculated as the amount of CNT produced, divided by the amount of PP used to produce it.

After production yields were assessed, the catalyst-combination yielding the highest amount of tubes was chosen to be used for the remainder of the work. The straight CNTs produced constituted 95% of the product and had diameters less than 30 nm. About 5% of the CNTs had double helical structures with diameters of 60 nm. It is important to note that the qualities of the produced CNTs are very good and TEM observations showed no sign of amorphous carbon. In addition, using TGA analysis, the degradation range of the synthesized products was found to be 600–800 °C peaking at 730 °C. These values are comparable to values for CNTs produced traditionally via the arc process. Also, only 0.3% of the material remained when temperatures rose above 800 °C, indicating very excellent purity. With the use of various catalysts it was noticed that when Ni was used alone, only straight CNTs were produced. Other research indicates that when Molybdenum-containing catalysts are employed helical products are seen [66]. Thus the researchers speculated that the existence of Mo might have led to the helical patterns they observed as well [63]. On the other hand, when producing CNTs from methane, if too high concentrations of Mo were used in the catalyst which contained Co and Mg as well, it would result in lower graphitized graphene walls and lower yields of CNTs [67].

Elsewhere, Chen et al. [68] were able to synthesize chestnut-like carbon nanotube spheres in a muffle furnace from the in situ heating of a mixture containing PP, OMMT, and nickel formate. In the process, nickel nanoparticles were produced in situ, which in turn acted as the catalyst in the autoclave-like microreactors formed by the OMMT. Interestingly, these Ni nanoparticles were speculated to be more active and useful in producing CNTs than pre-synthesized nickel nanocatalysts. The advantage of this set-up compared to some others is that in those studies pre-synthesized nickel nanocatalysts were crucial for CNT formation [59] whereas it is not the case here. It has been shown elsewhere that the diameters of CNTs are directly related to the size of the employed metal catalyst [69]. Nickel formate is known to dehydrate at 160 °C and decompose at 260 °C, followed by a self-redox reaction which produces gases and metallic nickel [70]. These nanoparticles in turn act as catalysts and result in the CNT morphology to be different from other studies.

In order to synthesize the CNTs, nickel formate was first dehydrated; then the components were fixed in a Brabender mixer at 80 rpm and 180 °C for 7 min; next, the mixture was placed in a muffle furnace and kept at 900 °C for five minutes; finally, the black powder was obtained by letting the mixture cool to room temperature. This black powder was in turn treated with hydrofluoric and aqueous nitric acid in order to remove the clay, amorphous carbon, and nickel. The treatments took more than 48 h.

Table 5
Summary of key studies utilizing muffle furnace reactors.

Reference	Polymer	Reactor type	Temperature (°C)	Pressure	Reaction time	Catalyst	Length of CNT	Diameter (nm)	Product description
[63,68,72]	PP	Muffle furnace	850		10 min	Ni(NO ₃) ₂ / (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O/ Mg(NO ₃) ₂		95% Straight and diameter less than 30 nm, 5% helical 60 nm diameter	Excellent quality CNTs. Mo is thought to be responsible for helical CNTs
			900	Autoclave-like micro-reactors formed by OMMT	5 min	OMMT and nickel formate OMMT, ferrocene and Co(Ac) ₂	Lengths in the micrometer range	Outer and inner diameters of 25–50 nm and 5–10 nm respectively 10–30 nm	CNTs tangled into chestnut-like balls with each other Exterior of the CNTs do not have a graphitic structure allowing easier modification of the products

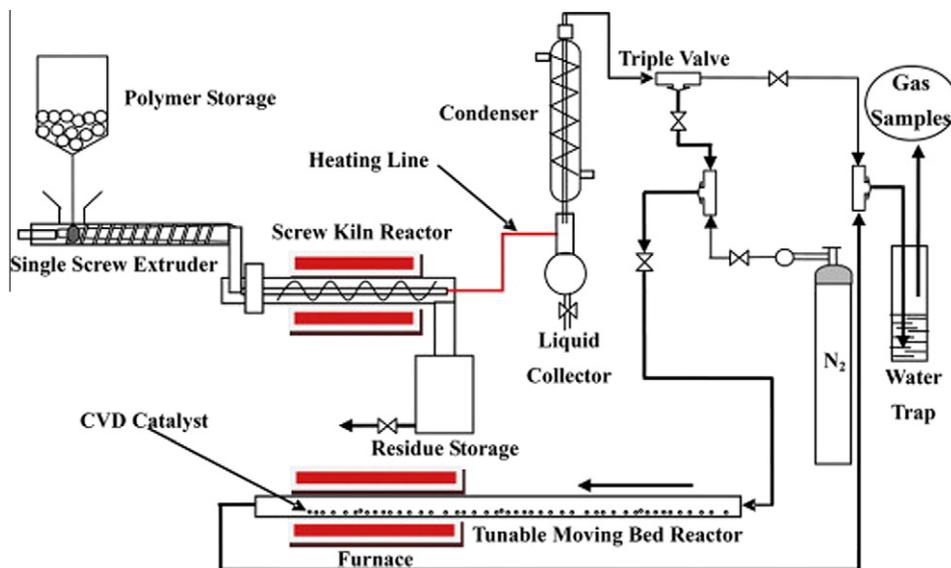


Fig. 2. Schematic diagram of the reaction system with the possibility of liquid product separation prior to CNT formation proposed by [74].

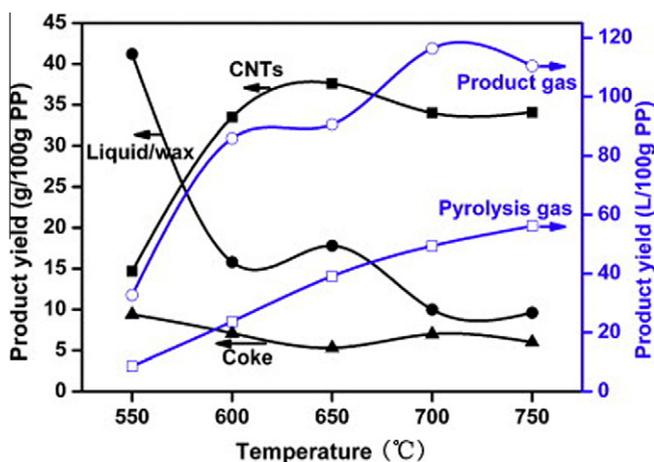


Fig. 3. Effect of the pyrolysis temperature (stage 1) on various yields in the two-stage system of [74] while the gas decomposition temperature (stage 2) is kept at 700 °C.

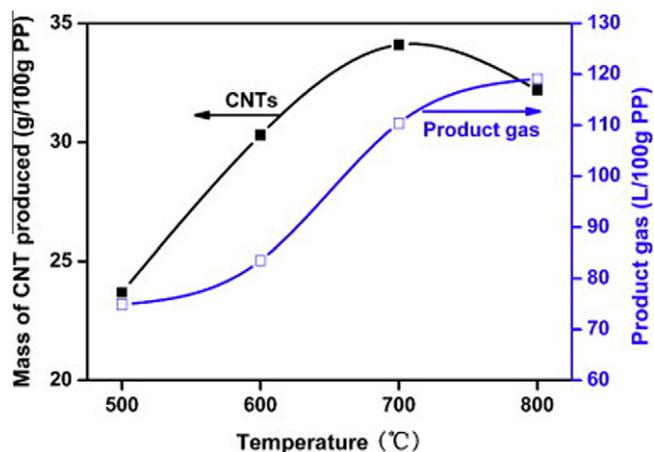


Fig. 4. Effect of the gas decomposition temperature (stage 2) on various yields in the two-stage system of [74] while the pyrolysis temperature (stage 1) is kept at 750 °C.

The resulting CNTs with lengths in the micrometer range, and outer and inner diameters of 25–50 nm and 5–10 nm respectively, are tangled into chestnut-like balls with each other. It was seen that heating times, heating temperatures, and in particular, the composition of the mixture strongly affected the CNT formation. The jumbled spheres are of the micrometer scale and can be separated with conventional filtration methods.

With the intention of assessing the applicability of the resulting product, Pt nanoparticles with mean diameter of 2.64 nm were successfully deposited on the CNTs to be used as catalyst supports. Also, N_2 adsorption–desorption experiments were carried out with agreeable results showing total surface and pore volume to be 250 m^2/g and 0.5877 cm^3/g respectively. The isotherms show typical type IV with a hysteresis loop, indicating mesoporosity. As mentioned before, the products were treated with acids after their synthesis. It should be noted that acid treatment must have had some effect on the high surface area due to the formation of hydroxy, carboxy, and carbonyl functional groups on the surface of the nanotubes [71].

In a more recent study, Chen et al. [72] melt-blended OMMT with PP and heated the obtained composite to 900 °C in a muffle furnace. They found that if a mixture of ferrocene and $Co(Ac)_2$ (weight ratio: 70/30) was used as a catalyst precursor, CNTs (diameters of 10–30 nm) would be produced with a yield of 18% (W_{CNS}/W_{PP}). The produced CNTs were seen to be randomly and loosely dispersed in the MMT platelets; different from the in situ or pre-synthesized catalyst approaches previously discussed. The researchers noted that easier dispersion in polymer matrices could be achieved with such morphologies leading to better applicability. About 64 wt.% of the produced CNT–MMT composite consisted of CNTs. It was also observed that the exterior of the CNTs do not have a graphitic structure which would allow easier modification of the products. Purification processes were used to successfully obtain pure CNTs. In TGA analysis in the presence of air, the CNTs decomposed in the range of 585–630 °C. If there was less ferrocene used in the ratio of catalysts, morphologies did not change, but CNTs yield diminished accordingly. If no ferrocene was used at all, the presence of $Co(Ac)_2$ resulted in the production of carbon nanospheres. Alternatively, when only ferrocene was used neither nanotubes nor nanospheres were obtained. A possible mechanism was also presented. The research group had previously elaborated extensively on the mechanism of CNT production in the presence

Table 6
Summary of key studies utilizing moving bed reactors.

Reference	Polymer	Reactor type	Temperature (°C)	Reaction time	Catalyst	Diameter (nm)	Product description
[74,75]	PP	Screw kiln (pyrolysis) + moving bed (synthesis)	500–800	Continuous process	Zeolite in pyrolysis, and NiO in synthesis	At 500 °C outer diameters were 10–50 nm, while at 800 °C they were 15–25 nm	The CNT quality and the mean inner diameter of the tubes increased with decomposition temperature.

of OMMT and nickel elsewhere [73]. A summary of various studies in which muffle furnace reactors have been used can be seen in Table 5.

6. Moving bed

In another very recent study, Liu et al. focused on not only CNT production from PP, but also on the production of H₂ as a valuable byproduct of the synthesis process [74]. As can be seen in Fig. 2, they devised a two-stage process for catalytic reactions to convert polypropylene (PP) into MWCNTs in the presence of H₂. First the PP was pyrolyzed in a screw kiln reactor in the presence of HZSM-5 zeolite catalyst; and after the liquid products were condensed from the resulting vapors, the pyrolysis gases were decomposed in a moving-bed reactor in the presence of a nickel catalyst. The advantage of using a NiO catalyst is that acid could be used to easily wash it off.

As seen in Figs. 3 and 4, the effects of operational temperatures for both the pyrolysis (first) and decomposition (second) steps of the process were examined. If the pyrolysis temperature was fixed at 750 °C, a decomposition temperature of 700 °C would yield the most CNTs. Alternatively, if the decomposition temperature was fixed at 700 °C, then the CNT production would reach its maximum at a pyrolysis temperature of about 640 °C. As pyrolysis temperatures rose, less liquids and more gases were produced. However, the MWCNT yield was a function of both the quantity and quality of the produced gases. Hydrogen and methane were the biggest constituents of the gas, followed by a small amount of CO and C₂–C₅.

The majority of the produced products were MWCNTs with hollow centers. As the temperatures were raised the diameter distribution of the tubes narrowed. At 500 °C the range of the outer diameters were 10–50 nm, while at 800 °C this range narrowed to 15–25 nm. However, the mean inner diameter of the tubes increased with temperature. Also, at 800 °C, higher graphitization was seen in addition to more perfectly parallel carbon layers. At 500 °C, the MWCNTs were not parallel to the tube axis and had fishbone-like graphic layers on the outside. TGA analysis was used to observe the oxidation temperature of the produced materials. It was seen that higher temperatures produced less defective samples with higher decomposition temperatures. It is thought that the CNTs are formed as carbon diffuses into the metal surface and in turn precipitates from the metal. The rates at which hydrocarbons decompose into solid carbon and diffuse are functions of the temperature. Thus diversity in temperature would naturally lead to various morphologies.

Previously, Liu et al. [75] had also have also conducted a study in which various ratios of Si/Al for the zeolite catalyst were examined in a very similar two-step process for the treatment of both virgin and waste PP. NiO was used for the moving-bed step. The NiO catalyst was utilized with no need of reduction since the hydrogen gas produced in the reactions would reduce the catalyst into Ni in situ.

The temperatures of the first and second steps of the process were fixed at 750 °C and 700 °C respectively and the plastic feed

rate was fixed at 80 g/h. When PP was used as feedstock, Si/Al molar ratios of 25, 38, and 50 lead to final CNT products with maximum oxidation weight loss (TGA) at 615.1, 601.4 and 590.9 °C correspondingly. Also, as the molar ratio increased, the production of hydrogen gas diminished. Under the best conditions, approximately 65 L of Hydrogen gas was produced per hour.

When waste PP (from car bumpers) was used MWCNTs with lower quality, more impurities such as amorphous carbon, and with a wider diameter distribution were found. The solid residue chars of the pyrolysis contained various elements which are thought to have come from fillers in the form of calcium carbonate, talcum powder or coupling agent of organic titanate. Although these products did not have flawless quality, in general, CNT defects can be distinguishably reduced with thermal annealing methods leading to highly graphitized products [76,77]. A summary of the key studies in which moving bed reactors have been used can be seen in Table 6.

7. Fluidized beds

Arena and Mastellone, alongside their colleagues, have presented a number of papers regarding the mass production of multi-wall carbon nanotubes by means of low-cost pyrolysis of various polyolefins in an atmospheric bubbling fluidized bed. In these experiments, in order to fluidize the bed, nitrogen gas was employed. The bed particles were quartz-rich sand or alumina. Online gas analyzers were used to recognize and quantify the hydrocarbon concentrations in the gas phase during the period of the experiment.

In one of their earlier work, the stability to thermal oxidation of the products was subsequently tested in air and it was seen that the main decomposition stage appeared at 690–700 °C [78]. Overall, this solid–gas fluidized technique allowed continuous operation under high heating rates, high exchange coefficients and reliable control over residence times. CNTs with diameters in the range of 15–40 nm were produced. Although, small amounts of other sizes could be seen, Arena et al. believe that the process conditions could be tuned to optimize the production claiming that both the mean length of the produced CNTs as well as their morphology (coiled and straight tubes) were compatible with commercial samples. Considering the cheap feedstock of the process, the low temperature compared to what is usually employed for CNT production, and the yield much higher than which is seen in traditional techniques, the overall process seems promising and cost effective.

Elsewhere, the researchers added more information and detail to their work [79–81]. They explained that the rapid contact between the gas and solid phase results in good mixing, increased fractional conversion, and almost uniform isothermal conditions allowing for reliable process control. The researchers showed that similar results were obtained when processing polyethylene, polypropylene, polyethylene terephthalate, as well as mixtures of these polymers. Both virgin and recycled feeds were used.

As far as how the CNTs are formed, the researchers speculated that upon the injection of polymers into the hot fluidized reactor

Table 7
Summary of various operational runs of fluidized bed CNT synthesis [81].

Polymer	Bed temperature (°C)	Bed particle mean diameter (µm)	Fluidizing velocity	MWCNT yield (g/g of polymer)
PP	700	140	U	Fullerenes
PE	700	140	U	Fullerenes
PP	500	140	U	0.07
PP	600	140	U	0.11
PE	600	140	U	0.16
PET	600	140	U	0.19
PP	600	252	U	0.22
PE	600	252	2U	0.32
PP	600	252	2U	0.51

the surface of the plastic pellets soften and attract and adhere to several bed particles. So an aggregate is formed having a solid polymer core with a solid external shell of bed particles. With the further increase of temperature, the outer surface of the polymer pellet melts and the polymer begins to flow forming a uniform coating of polymer over and between the external shell material. The polymers begin to crack after the coating has covered the bed particles. In the end, these covering layers are entirely strewn by nanotubes and nanofibers having diameters between 10 and 150 nm [79]. Experiments showed that a temperature lower than 480 °C resulted in the unwanted defluidization of the bed, whereas temperatures higher than 700 °C have no advantages in CNT yield and result in the formation of other nanostructures that could be identified as fullerenes [81].

The size of quartz bed particles and the fluidizing velocity at the bottom of the bed were also altered to distinguish their potential roles and significance. The operating conditions and their results are summed up in Table 7. It was found that increasing the bed particle diameter resulted in reduced quality of MWCNTs. The use of silica or alumina gave similar results to the quartz sand. The researchers also reported adding ferrous oxide to the bed but without positive results [81]. In their work, the researchers mistakenly referred to Fe₂O₃ as ferrous oxide. It was unclear whether they incorrectly referred to Fe₂O₃ as ferrous oxide, or, they had used ferric oxide instead. Through correspondence with the authors, it was cleared up that in fact ferric oxide (Fe₂O₃) had been used.

In one of their works which neglected to mention important details such as the feed or resulting materials' compositions, they varied the bed temperature in the range of 450–850 °C and the gas fluidization velocity in the range of 0.005–0.4 m/s [78]. However, the fluidizing velocity at the bottom entrance of the reactor was shown not to be of critical importance in MWCNT quality. The researchers argued that this could be due to the fact that the effective velocity throughout the bed is much higher than the fluidizing velocity as a result of large production of gas from the breakdown of the polymeric material [79]. The resulting materials were reported to be stable up to 590 °C which was lower than the previous claim made by the same authors [78].

Swartbooi and North [82] became aware of Arena et al.'s work in 2005 and decided to investigate and reproduce the reported

results. They noted that although they were able to produce CNTs with this method, the product was of poor quality with diameters in the range of 200–400 nm. Also, they found a high degree of buckling, amorphous carbon and other structural defects. Testing conditions were tweaked and better nanotubes in the diameter range of 100–200 nm were produced. Unfortunately, the study of using the plastic feedstock could not be satisfactorily pursued due to multiple operational issues related to the polymer feed. The researchers noted that the formation of sinters/agglomerates lead to the defluidization of the reactor and inhibited the process. Therefore the parametric study was not completed. In attempting to minimize the operational problems, Swartbooi and North went onto replace the waste plastics with carbonaceous gas, and found that ethylene gas as the feedstock improved the repeatability of the experiments.

Mastellone and Arena added to their findings in 2008 [83]. Tests were carried out at 600 °C as well as 800 °C. The interior wall of the reactor is constructed from a stainless steel Fe, Cr, Ni, and Mo. The current study reconfirms the catalytic behavior of these steel mesh metals – particularly Ni and Fe which had previously been identified as effective in CNT production [84–86].

Although PET should theoretically degrade completely by 550 °C, the researchers noted that at 600 °C a solid phase is still very much present and that a very viscous highly stable product is formed which hinders the fluidization. This caused the bed to defluidize after 1100 s of operation. Whence the operation was shut down, solid deposits were taken out and analyzed. At 800 °C, the synthesis of other quasi-spherical products was dominant compared to CNT yields. The composition of the products including the gases varied markedly from 600 °C. It was concluded that the solid phase containing CNTs was only produced in a certain time window of 2–4 h depending on the temperature. At higher residence times, the solid phase would be replaced by liquids. It was also concluded that the production of CO leads to the deactivation of the metal catalysts, and in turn, the inhibition of CNT synthesis [83].

In literature, the combination of utilizing a fluidized bed coupled with a CVD unit has also been considered. Yen et al. [87], did so by using polycarbosilane (PCS) and polyethylene (PE) as the carbonaceous source and impregnated MgO and Fe(NO₃)₃ as catalysts. The two furnaces were positioned in series. The lower furnace is in fact the bubbling fluidized bed, and the upper furnace the CVD unit. The temperatures of the lower and upper furnaces were 800–950 °C and 700–800 °C respectively. Argon and Hydrogen gas were chosen as carrier gases to keep the bed fluidized. The results obtained from the use of PCS will not be discussed in detail in this report. However, what can be said is that when comparing the differences between the use of PE and PCS, polyethylene yielded better quality CNTs with a higher extent of graphitization. The CNTs produced from PE had lengths as long as 1 µm and diameters of 25–90 nm. Results showed that greater graphitization is obtained when a higher ratio of hydrogen is used in the carrier gas. This is because the H₂ enhances the decomposition of PE to produce carbons which are then in turn formed into CNTs via the catalyst.

Table 8
Summary of key studies utilizing fluidized bed reactors.

Reference	Polymer	Reactor type	Temperature (°C)	Reaction time	Catalyst	Product description
[78–81,83]	PE, PP, PET	Fluidized bed	450–850	Continuous, process takes 2–4 h	Addition of ferric oxide had no positive effect. Internal walls of the stainless steel reactor act as catalyst	10–150 nm diameter depending on operation parameters
[87]	PE	Fluidized bed (lower) + CVD chamber (upper)	Lower and upper furnaces 800–950 and 700–800 respectively		Impregnated MgO and Fe(NO ₃) ₃	25–90 nm diameter with lengths up to 1 µm

Table 9

PP/PPMA/Inorganic Solid/ $\text{Ni}_2\text{O}_3 = 80/10/5/5$ except for the “blank” run which has no inorganic solid [73].

Inorganic solid	Yield of MWCNTs (wt.%) after purification
Blank	8
Na – ZSM-5	10.9
Na – MMT	15.6
H – ZAM-5	42
OMMT	44.8
NH_4 – MMT	56

Often the Raman Spectroscopy method is used to assess CNT quality. The various emerging bands indicate different structures. For example the ID band (at around 1343 cm^{-1} in the Raman spectra) indicates disordered carbon structures with dangling bonds inside the carbon layers, and the IG band associated with graphitization of CNTs (at around 1580 cm^{-1} in the Raman spectra) signifies a mode of hexagonal graphite indicating vibrations of sp^2 bonded carbon atoms in graphite [50,88]. So the smaller the ID/IG ratio is, the greater the degree of graphitization will be. However, although this method can be used for a good initial evaluation of the samples, it is a rough assessment of the disordered carbon due to the fact that the presence of graphitic carbon not in the form of CNT will skew the results [89]. A summary of the key studies in which fluidized bed reactors have been used can be seen in Table 8.

8. Not clarified

The team of researchers working with OMMT mentioned previously, also tried examining the various effects of using the clay alongside Ni_2O_3 on CNT production from polypropylene (PP) [73]. It could be guessed that this process was carried out in a normal pyrolysis furnace. But since the reactor type was not directly specified in the text, this study has been classified in this section. The combination of catalysts employed provided two kinds of catalytic reactions, the first being the catalytic degradation on PP, and the second being the catalytic carbonization of the degradation products. After the thermal decomposition of alkylammonium in the clay, MMT containing hydrogen protons will form on MMT layers. The H-MMT will act as a catalyst which assists the degradation of PP. A mixture of PP/PPMA/OMMT/ $\text{Ni}_2\text{O}_3 = 80/10/5/5$ (wt.%) was pyrolyzed at $700\text{ }^\circ\text{C}$ and MWCNTs with a yield of 44.8 wt.% were obtained after extensive purification. The synthesized tubes had graphite layer sidewalls which were not always concentric. During the TGA analysis, oxidation began a little under $500\text{ }^\circ\text{C}$ and reached its maximum at $560\text{ }^\circ\text{C}$. Although these figures are good enough to declare relative purity of the products, they are nevertheless indicative of faults and defects compared to values obtained in literature from other CVD processes [90].

Subsequently, as can be seen in Table 9, a variety of combinations and mixtures were tested to see the influence of Brønsted acid sites (solid acids) on MWCNT yield.

Interestingly, the researchers also tried breaking the process down into two distinct steps in which OMMT and Ni_2O_3 have no contact with each other. Under those conditions, yields are dramatically reduced. It is thought that the combination of the two catalysts in a single step might promote the formation of carbon products (C1–C3 hydrocarbons) which are then more easily synthesized into nanotubes. With one-pot process which supports the creation of carbenium ions, higher carbon molecules are promoted to convert to nanotubes due to the hydride-transfer reaction. This is greatly advantageous because generally, molecules with higher carbon numbers which are the traditional products of the uncatalyzed thermal degradation of PP and other plastic polymers, have a more difficult time transforming into nanotubes.

9. Discussion

As seen throughout the review, there are various methods and conditions under which CNTs have been produced from plastic feedstock. The growth conditions, catalysts, substrates, and resulting CNT quality, yield, and diameters all vary. There exists an immense number of variables each of which potentially affects the CNT production. What makes the distinction of patterns regarding various effective parameters much more difficult is that many of them are interdependent. Due to the high number of variables and the limited number of papers available in the field much more work remains to be done.

Through the various studies, one of the main observations is the effect of catalyst compositions, sizes, and feeding ratios on the final synthesized product. In most studies, at the lower temperatures, CNT diameters are in direct relation with catalyst particle size. However as temperatures rise to $800\text{ }^\circ\text{C}$ and beyond, the coalescence of catalysts makes their initial size rather irrelevant. Kukovitsky et al. [33] indicated that the size of the Ni catalyst remained significant only up to $700\text{ }^\circ\text{C}$. Meanwhile, the iron nanocatalysts employed by Chung and Jou [35] showed how efficient the reduction of catalyst size could be. In fact, this study employed the least amount of catalyst compared to all other studies investigated in this report. The morphology seemed to be governed by the competitive processes between catalyst coalescence and CNT growth. The method with which the precursors were prepared could also have an effect. Also very important, might be the fact that the process was carried out under vacuum conditions. If reducing catalyst usage is a goal, it seems worthwhile to investigate the importance of the parameters in this process. The remarkably low amount of catalyst used here, was one hundred-fold less than some others [37]. Jou and Hsu [91] had previously used small amounts of the same catalyst, again spun coated onto silicon wafers, in a vacuum pyrolysis to produce CNTs from polycarbosilane.

Although Yang et al. [37] did use a large amount of catalysts, nevertheless, they were successful at producing the longest CNT arrays from among the literature; with an average growth of $12\text{ }\mu\text{m}/\text{min}$ and lengths of up to $500\text{ }\mu\text{m}$ after 40 min. These figures are markedly lower than growth rates regarding other CVD processes for producing carbon nanotubes (for example $\sim 50\text{ }\mu\text{m}/\text{min}$ reported by Zhang et al. [39]), but at the same time, they are within an acceptable range much higher than the other studies investigated in this review. Also as previously mentioned, the advantage of Yang et al.'s process compared to others is that the obtained products are vertically aligned.

The combination of catalysts employed for a particular process is also of interest. Time and time again, it was seen that a single catalyst would be many-fold less effective than when it was employed with other precursors and/or catalysts. The most evident example might be the work of Song and Ji [63] who demonstrated a more than 50% growth of CNT yield (wt.%) when a combination of Ni, Mo, and Mg catalyst was prepared and used instead of only Ni. The process for preparing the catalysts was so effective, that it took only ten minutes to obtain the best quality CNTs reviewed in this report, with yields as high as 58%. The TGA analysis showed the degradation range to be comparable to CNTs produced traditionally via the arc process. None of the other studies even came close to this quality of products, with the next product decomposing more than $100\text{ }^\circ\text{C}$ earlier. Also, only 0.3% of the material remained when decomposition temperatures rose above $800\text{ }^\circ\text{C}$, indicating very excellent purity.

The highest yields seen in this review were obtained by Kong and Zhang [47] who obtained a yield of 80% of CNTs with diameters from 20 to 60 nm from PE in an autoclave at $700\text{ }^\circ\text{C}$. Although the quality of their product changed, they were able to repeat such

high yields after altering their feed and catalyst in the process. This might indicate that the process operating conditions might have played the most important role in the high yields. The problem with this proposed method is that it takes much too long to produce the CNTs (over 12 h) and much more to purify them.

The presence of oxygen is also a point of interest. Pol [52] reported that an inert atmosphere within the autoclave reactor produced 10–15% more nanoproducts compared to when air was present. They continued to explain that this was because in the presence of air, some of the carbon would react with the oxygen in the air and not be readily available to transform into nanoproducts. On the other hand, Zhuo et al. [40] reported that when they incorporated a combustion step before CNT formation which introduced CO and CO₂ into the system, better CNT growth was achieved. The presence of H₂ and H₂O were also favorable. Although these two findings might seem contradictory at first, it is not necessarily the case. If a closer look is taken, one can see that in Zhuo et al's work, the amount of oxygen is very much regulated meaning that an ample amount of carbon is let through into the CNT synthesis step without ever coming into contact with the air. Therefore, there is no carbon deficit for CNT formation. However, in Pol's set-up, the oxygen within the autoclave cannot be regulated or controlled, and hence, it is more impeding than helpful. A modification to Pol's work, for example having a limited amount of oxygen alongside the majority inert atmosphere within the autoclave, might improve results. Also, if plastics which inherently contain oxygen (such as PET) are used as feeds, the small amount of oxygen could automatically be provided.

It is noteworthy that most of the reviewed studies in this report use virgin plastics as their feed. In addition, plastics are used separately and not as mixtures like they would be found in waste streams. Thus these feeds are not representative of waste plastic streams. Although researchers have mentioned time and time again that the research could ultimately be used for that goal, it has not been so in most cases. Zhuo et al. [42] reported that no major differences in morphologies was seen between products from HDPE and LDPE. Also, no major difference was seen between pre- or post-consumer PE feedstock. Nevertheless, the products from various feeds are different when it comes to diameters, wall thickness, degree of graphitization, and so on. If a holistic process is to be developed, the impurities of various plastics could not be overlooked as Liu et al. [75] also indicated that when waste PP from car bumpers (including impurities) was used, more impurities such as amorphous carbon and a wider diameter distribution were found. Also, the Cl in PVC has been shown to eventually poison the catalyst and result in more entangled dense CNT arrays [37]. Nevertheless, huge areas of potential research exist in order to examine the various plastic feed conditions and effects.

To the authors of the review, the most interesting reactor set-ups to be pursued for further investigation are the quartz tube reactor employed by Zhou et al. [40,42] as well as the moving bed reactor employed by Liu et al. [74,75]. Both these experimental set-ups synthesize CNTs from CVD. The set-up of [40,42] claims to be self-sustaining and has short operation times. Various plastics have been tested and a cursory examination of the morphologies of the produced CNTs showed no major difference between products from milk jugs (HDPE) and newspaper wraps (LDPE). Also, no major difference was seen between pre- or post-consumer PE feedstock. These are all important reasons which make this option very attractive for possible scale-up. Since this method is rather recent, there is a lot of prospective work to be done regarding operating conditions and characterization. The authors believe that with some work, a continuous process set-up could be developed from this method. On the other hand, the set-up of [74,75] already has the tremendous advantage of being verified as a continuous process. In addition, an encouraging observation is that when a

two-step system is utilized where the plastic feed is first pyrolyzed in one chamber, and the effluent gas is subsequently synthesized into CNTs in another section, the liquid product could be extracted from the system and utilized elsewhere. Many studies have been conducted in recent years which aim to produce liquid products such as diesel and petroleum from plastic waste pyrolysis [93,94]. From a process perspective, the fact that the production of liquid products could be pursued alongside CNT synthesis from the gas effluents is an ever-so-important advantage which has yet to be considered by any researcher. In addition, since plastic pyrolysis is an exothermic process, if the produced energy is correctly harnessed and utilized, it may be enough to provide the requirements of the subsequent steps of CNT production [40]. Hydrogen production is also another benefit not to be neglected.

10. Conclusion

Various processes have been presented for the production of carbon nanotubes from plastics as carbonaceous feeds. The increasing problem of waste streams, coupled with the potential benefits and profits coming from CNTs has made the possibility of producing these high value products from the seemingly useless waste stream attractive. The findings of literature show that such an endeavor is achievable through a large variety of reactor types and process set-ups. The present report is the first review to ever summarize the existing literature in this regard. Due to the limited number of studies present, there are many various aspects which are still left open for future work. Nevertheless, the most promising findings are indicated and the results of some processes are compared. In addition, areas which seem to require more investigation are touched upon.

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