1. Introduction

Nanotechnology products were responsible for a consumer market of about US$ 11 trillion in 2010, wherein US$ 340 billion correspond just to nanomaterials (CNMs). Nanomaterials consist of structures with at least one dimension in the order of nanometers \((1 \times 10^{-9} \text{ m})\). The most popular nanomaterial is the carbon nanotubes, which consist of coaxial tubular graphene sheets. CNMs have extraordinary mechanical, thermal and electrical properties. Such characteristics provide a wide range of potential applications in...
energy management, electronics, structural materials and chemical processing\cite{10}. However, the high cost to produce CNMs limits their usage. To decrease the cost of these materials, it is instrumental to reduce the expenses associated with the procurement of raw-materials and to reduce production expenses. By using carbonaceous solid wastes as feedstocks for CNMs growth, the cost of raw-material can be minimized. Furthermore the process operating costs can be minimized by burning additional waste to provide thermal energy\cite{9}.

Aside of the carbon sources for nanomaterials 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\cite{6} or fixed substrate-based\cite{7} configurations. Effective catalysts include, but are not limited to, iron (Fe)\cite{8}, nickel (Ni)\cite{9}, and cobalt (Co)\cite{10}. Alloys that incorporate such elements in their compositions, e.g. stainless steel, have also been examined\cite{11}. Particularly, stainless steel meshes have served as substrates, coated with a thin film of extra catalyst such as Ni\cite{11}. This finding is important since use of stainless steel, a readily-available and economical commodity, can lower the cost of CNMs production. This study utilized AISI 304 stainless steel meshes as both catalysts and substrates for growing nanomaterials.

Stainless steels are alloys with a minimum of 10.5% chromium, which is necessary to form a stable passive film. This film protects the material against mild atmospheric corrosion. AISI 304 is an austenitic stainless steel that has high content of chromium (18%-20%) and nickel (8%-10.5%). This is the most used stainless steel alloy, available in a wider range of products, forms and finishes\cite{12,13}.

2. Methods

2.1 Raw Materials

The raw materials used in this study were: (i) waste tires obtained from a local source in the form of chips without metallic belts; (ii) pieces of post-consumer PET bottles; (iii) corn-derived Distillers Dried Grains with Solubles (DDGS) provided by a North American ethanol-producing company, which was used as received (grains about 500 μm, in diameter); (iv) sugarcane bagasse provided by a Brazilian ethanol producing company, which was received in fiber form and was pulverized to particle sizes smaller than 500 μm using a household blender. Table 1 lists the chemical composition of these materials determined by X-ray Fluorescence Spectroscopy and Elemental Analysis (CHN).

<table>
<thead>
<tr>
<th>Material</th>
<th>C (wt%)</th>
<th>O (wt%)</th>
<th>K (wt%)</th>
<th>H (wt%)</th>
<th>S (wt%)</th>
<th>N (wt%)</th>
<th>P (wt%)</th>
<th>Ca (wt%)</th>
<th>Fe (wt%)</th>
<th>Si (wt%)</th>
<th>Others (wt%)</th>
</tr>
</thead>
<tbody>
<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>4.6</td>
<td>—</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>
<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>PET</td>
<td>62.6</td>
<td>31.8</td>
<td>—</td>
<td>4.7</td>
<td>—</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.8</td>
</tr>
</tbody>
</table>

2.2 Methodology

Experiments were conducted in a laboratory-scale apparatus consisting of two furnaces in series, separated by a gas mixing section. The process for this waste-to-CNM generation consists of three steps. In the first step, batches of solid feedstock (4 g of DDGS or bagasse samples, 1 g of 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°C to 1,000°C. In the second step, the feedstock pyrolyzates were channeled through a mixing venturi to the second furnace at 1,000°C, which worked as synthesis reactor. Oxygen was introduced to the venturi empirically only in the cases of feedstocks with high carbon content in their composition (tires and PET), according to the necessity shown by past researches\cite{15,16}. A ceramic barrier filter was placed after the division of the two sections of the apparatus in order to prevent particulate matter from entering the synthesis chamber. In the third step, the burned effluents of the feedstocks entered the synthesis reactor where the catalyst was placed. A schematic of the process is shown in Fig. 1.

2.3 Catalyst

The catalyst system used in this work consisted of a mesh screen made of stainless steel type 304, which has chemical components according to ASTM E2016 specification: Cr (18%-20%), Ni (8%-10.5%), Mn (≤2%), Si (≤1.0%), N (≤0.1%), C (≤0.08%), P (≤0.05%), S (≤0.03%), and Fe (balance)\cite{14}. 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 about 40 mm, and were inserted in the quartz tube section of the second furnace.

2.4 Characterizations

LHCs generated during the experiments were monitored offline 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. 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 (i.e., without meshes) were also performed and the composition of the generated gases was likewise analyzed.

Morphological analysis of catalyzed materials was performed using Scanning Electronic Microscopy (SEM) and
Fig. 1  General demonstration of the process: (a) wastes are inserted into the furnace; (b) the filter retains the solid particles; and (c) gases come in contact with the catalyst.

Transmission Electron Microscopy (TEM). Random pieces of the mesh were removed and were placed directly on the SEM imaging stage (Fig. 2 shows the material collection for analysis). SEM analyses were conducted on a Hitachi 4800 instrument, at 3 kV voltage, and a working distance of 8.2 mm. For TEM samples, the meshes were sonicated in a 100% ethanol solution and the product were analyzed in a TEM instrument model JEOL 1010, with an accelerating voltage of 70 kV.

3. Results and Discussion

3.1 Analysis of Gas Emissions

The pyrolysis/combustion process of the wastes generated several light hydrocarbons (LHCs). Mole fractions of the most prominent LHCs detected in the experiments are shown in Fig. 3; data was collected with and without the catalyst system (the values are listed in parts per million – ppm). The most prominent LHCs species detected in this work included methane (CH₄), acetylene (C₂H₂), benzene (C₆H₆), and ethylene (C₂H₄). Traces of other compounds were also detected: toluene, ethane, propylene, propyne, ethylacetylene, and ethylbenzene[17].

![Graphs showing emissions of the most prominent LHCs with and without catalyst for Bagasse, DDGS, Tires, and PET.]

Fig. 3  Emissions of the most prominent LHCs (in ppm) detected in the experiments, with and without catalyst.

3.2 Discussion about the Catalyst System

A noteworthy trend emerging from the results of Fig. 3 is that all detected light hydrocarbon species were partially depleted at the presence of stainless steel meshes. The catalyst system induced thermal dehydrogenation reactions. Baker et al.[18,19] 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\(^{20}\). Eq. (1) illustrates this process, in which carbon and \(H_2\) are formed from hydrocarbons\(^{21}\).

\[
C_xH_y \rightarrow xC + \frac{1}{2}yH_2 \tag{1}
\]

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, which explains the mesh weight increase detected after the experiments.

Several prior studies have shown that the hydrocarbons produced in this work can be used as important carbon donors in the production of nanomaterials: methane\(^{22}\), acetylene\(^{23}\), benzene\(^{24}\), and ethylene\(^{25}\).

### 3.3 Microstructural Analysis of Produced Materials

Fig. 4 shows the SEM and TEM images of the synthesized nanomaterials on the surface of stainless steel screen through the use of different wastes as raw materials. In general terms, SEM images show entangled nanomaterials which cover not uniformly the catalyst mesh under all conditions. The images exhibit the catalyst meshes in the background and ramifications of nanomaterials impregnated in the surface. This fact confirms the previously proposed theory, in which the nanomaterials are formed in the solid particles of carbon that were precipitated on the metal surface. The following are presented weightings about results obtained with each waste used as feedstock.

#### 3.3.1 Sugarcane bagasse

SEM images of nanomaterials synthesized from sugarcane bagasse show cylindrical nanomaterials covering the catalyst surfaces. This sample was produced at process temperatures of \(1,000^\circ C\) for both the pyrolysis and synthesis reactors. Nanomaterials are in the form of well-separated, long (-50 \(\mu m\)), straight and smooth-surface cylinders with diameters in the range of 20 nm to 80 nm. In the case of bagasse, TEM images show that the produced cylindrical materials have tubular forms, which are characteristic of carbon nanotubes (CNTs)\(^{2,3}\).

#### 3.3.2 Corn-based DDGS

Experiments that used DDGS as a feedstock generated large populations of nanomaterials that completely cover the catalyst meshes. This sample was produced at process temperatures of \(1,000^\circ C\) for both the pyrolysis and synthesis reactors. Produced materials have twisted and crooked forms with irregular shapes and rugged surfaces. These nanomaterials resemble ropes with widths of 100 nm to 200 nm and lengths of about 50 \(\mu m\). In the case of DDGS, TEM images show that carbon nanomaterials were produced in the form of rugged and dense rope-like structures, which are characteristic of carbon nanoropes (CNRs)\(^{3,26}\).

#### 3.3.3 Unserviceable tires

SEM images of nanomaterials synthesized from tires exhibit upshots of nanomaterials originating from the surface of the catalyst substrate. This sample was produced at process temperatures of \(1,000^\circ C\) (pyrolysis and synthesis reactors), and with an addition of 19% \(O_2\) in the \(N_2\) atmosphere. Produced materials were in the form of long and often entangled cylinders with lengths of about 40 \(\mu m\), and widths of about 100 nm. TEM images of the materials produced from waste tires showed braid-like long CNMs with widths of 100 nm, in agreement to SEM observations\(^{2,27}\).

#### 3.3.4 Post-consumer PET bottles

The SEM images of nanomaterials synthesized from PET reveal the existence of cylindrical structures grown on the surface of the substrate catalyst. The lengths of these structures were typically 20 \(\mu m\) and the diameters were in the range of 50 nm to 200 nm. This sample was produced at process temperatures \(600^\circ C\) (pyrolysis reactor) and \(1,000^\circ C\) (synthesis reactor), and with an addition of 15% \(O_2\) in the \(N_2\) atmosphere. TEM images of the product synthesized from PET showed the formation of nanofibers (CNFs) with diameters of 90 nm to 140 nm\(^{28,29}\).
The related solid wastes may be used as feedstocks for CNM synthesis due to their high carbon content. However, the other elements presented in the chemical composition (Table 1) affect the generated gases (Fig. 3), which in turn affect the properties of CNMs in terms of structural architectures and dimensions. Furthermore, some of the used wastes contain minerals (sulfur, phosphorous, and zinc), which may have remained in the bottom of the pyrolysis reactor, as solid residuals. The temperatures used in this study (up to 1,000°C) are higher than the boiling points of the abovementioned minerals (S = 445°C; P = 280°C; Zn = 906°C). Therefore, some of the minerals may vaporize and enrich the gaseous reaction streams, which have individual effects on CNMs formation.

4. Conclusions

Nanomaterials, including carbon nanotubes, were successfully catalytically synthesized on AISI 304 stainless steel meshes using solid wastes as carbon donors. The controlled burned of the sugarcane bagasse, corn residue (DDGS), scrap tires, and post-consumer PET bottles generated several gaseous hydrocarbons, mainly methane, acetylene, benzene, and ethylene. The carbon content of these gases was catalytically converted into nanomaterials by the AISI 304 stainless-steel meshes, which may be proved by the reduction on the gaseous emissions and the mesh weight increase. Several types of CNMs were produced (nanotubes, nanofibers, and nanoropes), which were determined by the feedstock used. The produced nanomaterials presented lengths of 20 μm to 50 μm and diameters in the range of 20 nm to 200 nm. Therefore, at high temperature (~1,000°C), the AISI 304 stainless steel was shown to be an effective low-cost catalyst for nanomaterials generation through a two-step growth mechanism.

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References

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